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Compendium of Selected Methods for Sampling and Analysis at Geothermal Facilities

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The establishment of generally accepted methods for characterizing geothermal emissions has been hampered by the independent natures of both geothermal industrial development and sampling/analysis procedures despite three workshops on the latter (Las Vegas 1975, 1977, 1980). An independent study of the field has resulted in a compilation of the best methods for sampling, preservation and analysis of potential pollutants from geothermally fueled electric power plants. These methods have been selected as the most usable over the range of application commonly experienced in the various geothermal plant sample locations. In addition to plant and well piping, techniques for sampling cooling towers, ambient gases, solids, surface and subsurface waters are described, Emphasis is placed on the use of sampling probes to extract samples from heterogeneous flows. Where possible, analytical methods capable of reaching "aquatic life criteria" sensitivities are described. This series of techniques is best if applied, or directly monitored, by one person to optimize consistent use and interpretation. Certain sampling points, constituents and phases of plant operation are more amenable to quality assurance improvement in the emission measurements than others and are so identified.

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PREFACE

The methods described in this report were selected based on an evaluation of existing options, reviews by numerous practitioners, past experience, and information in the literature. The selected methods are not necessarily "standard methods."

For additional information, the following reports from earlier work are available:

GEOTHERMAL FLUID SAMPLING/ANALYSIS

- Kindle, C. H., and Woodruff, E. M. 1981. Techniques for Geothermal Liquid Sampling and Analysis. PNL-3801, Pacific Northwest Laboratory, Richland, Washington.
- Watson, J. C. 1979. Sampling and Analysis Methods for Geothermal Fluids and Gases. PNL-MA-572, Pacific Northwest Laboratory, Richland, Washington.

GROUNDWATER MONITORING

- Weiss, R. B., et al. 1979. Ground Water Monitoring Guidelines for Geothermal Development. EPA-600/7-79-218, U.S. Environmental Protection Agency.
- Geraghty and Miller, Inc. 1977. Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities. EPA-530/SW-611, U.S. Environmental Protection Agency.

These documents are available from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161. Furthermore, the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nevada, is currently performing research on groundwater monitoring and may be a source of additional information.

This document is a compendium of useful methods for sampling and analysis of geothermal fluids. It is not meant to be a monitoring strategy nor in any way suggest deviations from existing EPA regulations regarding discharge to the environment.

ABSTRACT

The establishment of generally accepted methods for characterizing geothermal emissions has been hampered by the independent natures of both geothermal industrial development and sampling/analysis procedures despite three workshops on the latter (Las Vegas 1975, 1977, 1980). An independent study of the field has resulted in a compilation of the best methods for sampling, preservation and analysis of potential pollutants from geothermally fueled electric power plants. These methods have been selected as the most usable over the range of application commonly experienced in the various geothermal plant sample locations. In addition to plant and well piping, techniques for sampling cooling towers, ambient gases, solids, surface and subsurface waters are described. Emphasis is placed on the use of sampling probes to extract samples from heterogeneous flows. Where possible, analytical methods capable of reaching "aquatic life criteria" sensitivities are described. This series of techniques is best if applied, or directly monitored, by one person to optimize consistent use and interpretation. Certain sampling points, constituents and phases of plant operation are more amenable to quality assurance improvement in the emission measurements than others and are so identified.

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1.0 INTRODUCTION

1.1 OBJECTIVE

This report is a compilation of the sampling and analysis methods for characterizing environmental contaminants that may be generated from a geothermal power plant. The specific goal of this document is to identify and suggest the best methods for geothermal plant situations, and their functional equivalents, while describing enough of the problems and variables to instruct the user on practical procedures.

1.2 SCOPE

The techniques described in this report address the sampling, preservation, and analysis of inorganic constituents of geothermal fluids which may be of environmental concern. These constituents and parameters include:

- general - alkalinity, specific conductance, total dissolved solids, pH
- anions - chloride, fluoride, nitrate, sulfate, sulfide
- metals - aluminum, arsenic, barium, boron, cadmium, chromium, copper, lead, lithium, manganese, mercury, molybdenum, selenium, silica, silver, zinc
- gases - radon, ammonia, hydrogen sulfide.

The techniques are described to permit sampling at all known emission locations at geothermal plants as well as the input to the plant. Although input to the plant would not represent an emission point, the techniques for sampling discussed here will permit a constituent mass balance through the plant to be calculated. Methods for sampling groundwater and ambient air are described in less detail since these techniques are not specific or unique to geothermal facilities and, in fact, may detect contributions that are nongeothermal in origin.

This manual does not represent policy implications regarding environmental monitoring practices or appropriate responses to environmental damage, whether actual or potential. Instead, the purpose of the report is strictly to serve as a technical "how-to" guide. Since the environmental regulation of geothermal plants is performed on a local basis, there is no intent here to suggest how the data should be interpreted.

1.3 DISCUSSION

The problem of ensuring data of known quality regarding geothermal emissions has not always been adequately addressed. For geothermal situations, quality assurance programs should emphasize sampling and field activities which are usually the major source of variance in the entire analytical process. The entire characterization approach, from sampling to data reporting, should be the responsibility of one knowledgeable person. It is expected that this person will be able to demonstrate the effective balance, for a particular plant, between good sampling practices and accurate analytical results. This viewpoint is incorporated in this report by the way the two parts of any characterization - sampling and analysis - are described.

The analytical procedures are described in a fairly standard format showing normal steps, precision, and sensitivity. The sampling techniques are described in a more general manner, sometimes suggesting steps that "should" be taken. It is the intent that the user shall identify the potential sampling problems at a particular plant and test their significance while utilizing the recommended methods. This approach will generate hard data relating to sampling uncertainties at the plant and will prove valuable in arriving at a proper sampling/analysis balance for the quality assurance program at a particular facility.

Underlying this approach is the assumption that the plant's chemical monitoring program will be the responsibility of one or more specialists. This assumption is consistent with industry practice to date, and it is to these persons that this report is addressed.

The methods incorporated into this report were selected through an evaluation of the practices in use in the geothermal area. The methods were initially evaluated based on consultations with numerous practitioners, as well as literature results and first-hand experience. Not all of the recommended methods are "standard methods." The recommended sampling techniques and equipment were found to be capable of extracting a representative sample with reasonable simplicity under the conditions described. All of the equipment is durable and should provide routine service for an extended period of time. The recommended analytical methods are suitable for analyzing the particular type of sample described based primarily on sensitivity, interference resistance, availability, and ease of operation.

2.0 SAMPLING

There are two overriding problems in geothermal plant flow sampling:

1. heterogeneous (two-phase) flow
2. composition shifts.

The heterogenous flow problem is addressed in this text by suggesting that the flow be separated into two single-phase streams before sampling. A method is given for sampling two-phase flow directly, but it is imperative that this method be used as described to generate data that would give an indication of possible errors. This recommendation is a specific extension of the discussion in the Introduction on achieving a balanced quality assurance approach.

Composition shifts can occur as a result of:

1. bringing different geothermal wells on line
2. changing flow rates
3. different flow histories.

All wells at a particular plant should be characterized. The composition may change with flow rate if the well draws from more than one zone having differing production characteristics. Limited data suggest that, except for long-term changes relating to reservoir conditions, the fluid composition of a given well is fairly constant once it has flowed for more than a day at a substantial production rate. Because of disposal limitations, it may be impractical to flow a new well for very long, so care should be taken during analysis and data interpretation not to mistake possible drilling residues for geothermal constituents. The problem of composition shifts due to reservoir conditions or flow histories is judged to be fairly minor and is not discussed further.

The range of geothermal plant sampling areas includes incoming steam lines; brine pipes; off-gas vents; cooling tower emissions; sludges of various origins; and piping and vessels of different size, location, and accessibility. The procedures for performing this sampling are described in a manner to suggest possible problems that might be encountered.

Reconstructing the composition of a geothermal fluid requires measurements of brine chemistry and analyses of separated brine, steam condensate, and gas phases. Samples from each phase are necessary because the fluids may not be in equilibrium at the sampling points. For quantitative retention of components, the sample, whether physically separated into two phases or not, must be cooled sufficiently to condense certain volatiles and water vapor. The collection and analysis schemes presented here are designed to allow complete liquid and gas analyses of potential pollutant species. Figure 2.1 is an overview of the

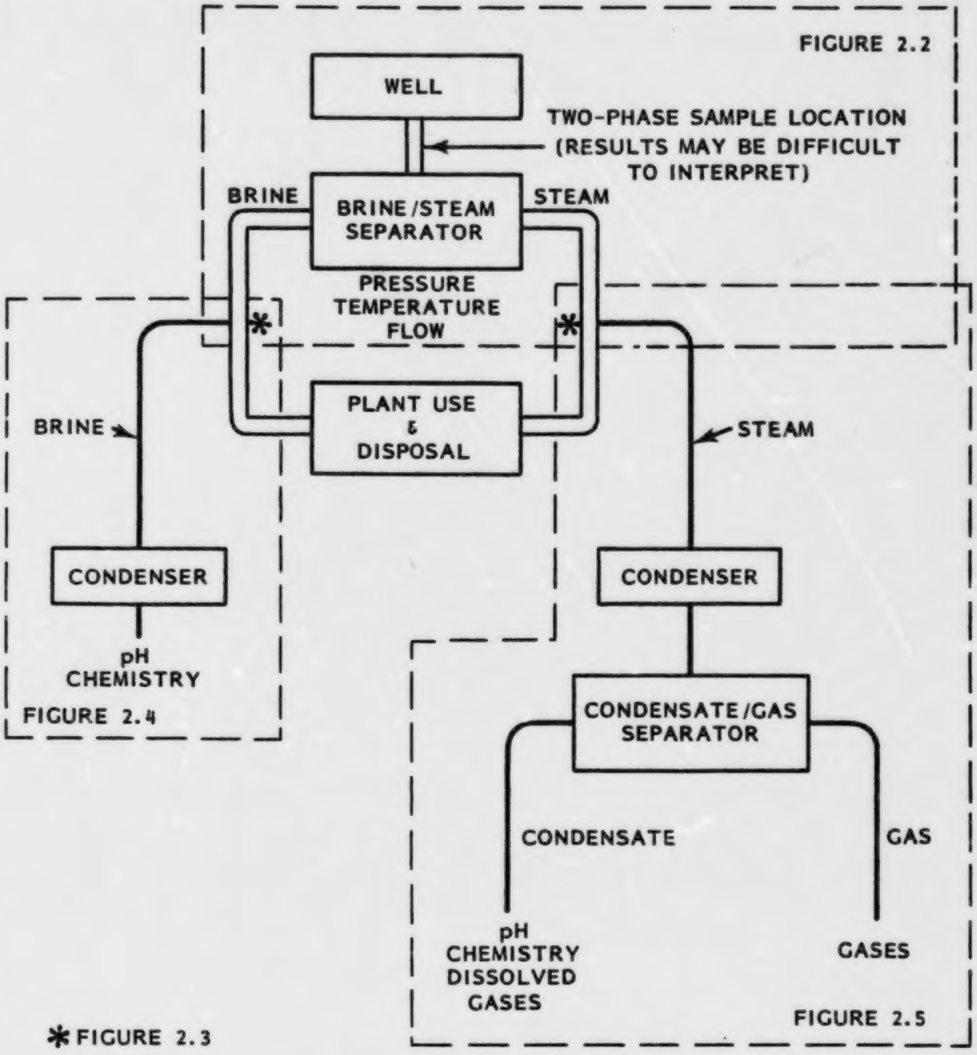


FIGURE 2.2
WELL
TWO-PHASE SAMPLE LOCATION (RESULTS MAY BE DIFFICULT TO INTERPRET)
BRINE
BRINE/STEAM SEPARATOR
STEAM
PRESSURE
TEMPERATURE
FLOW
PLANT USE & DISPOSAL
BRINE
STEAM
CONDENSER
CONDENSER
pH
CHEMISTRY
FIGURE 2.4
CONDENSATE/GAS SEPARATOR
CONDENSATE
GAS
pH
CHEMISTRY
DISSOLVED
GASES
GASES
FIGURE 2.5
* FIGURE 2.3

FIGURE 2.1. Geothermal Fluid Sampling Approach Showing Relationship of Subsequent Figures

processes used for examining well samples at selected collection sites. These processes and sample sites (Figure 2.1) are described in the following sections.

2.1. GEOTHERMAL WELL SAMPLING

2.1.1 Sample Site Selection

Typical wellhead sampling site locations are shown in Figure 2.2. Sampling points should be selected as far upstream (nearest the wellhead) as practical if a full flow separator is not used. Under actual field conditions, the choices of sampling locations are usually limited to those already built into the flowing well system. These locations could include access points for temperature, pressure, and other probe locations as well as fluid sampling positions.

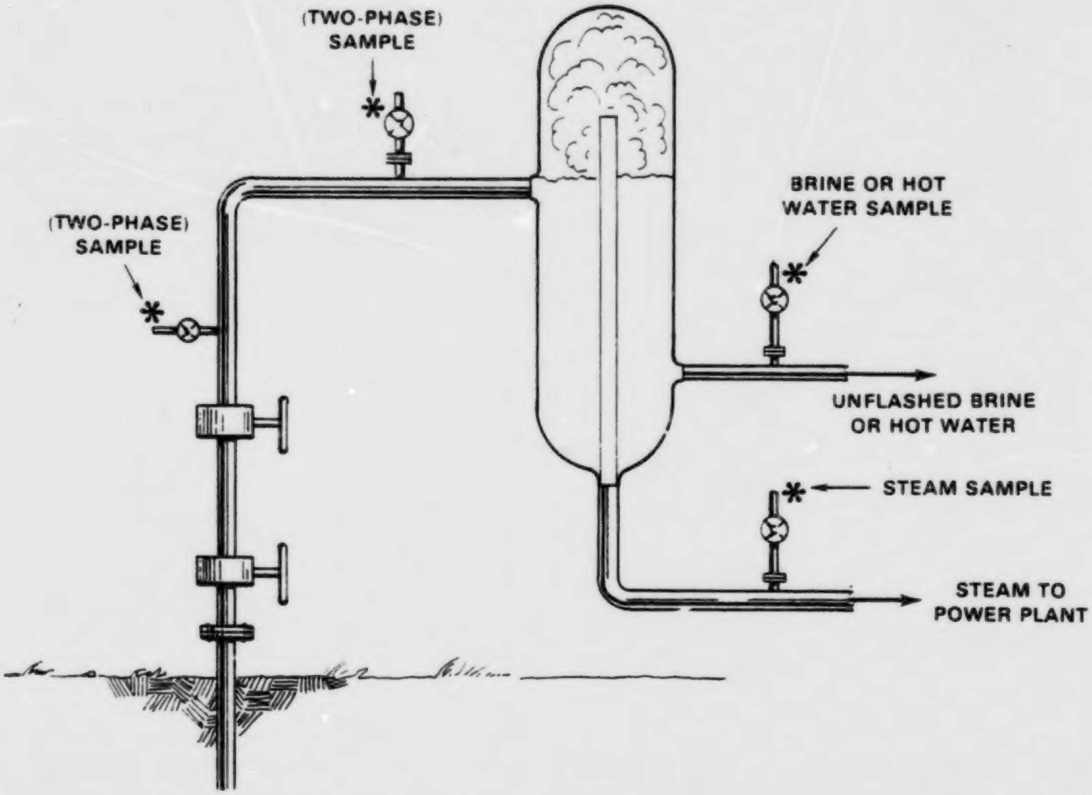

(TWO-PHASE) SAMPLE
(TWO-PHASE) SAMPLE
BRINE OR HOT WATER SAMPLE
UNFLASHED BRINE OR HOT WATER
STEAM SAMPLE
STEAM TO POWER PLANT

FIGURE 2.2. Sampling Scheme at a Typical Geothermal Wellhead and Steam Separator

In a dynamic system, maximum turbulence in fluid flow occurs within well piping after significant direction changes and in zones following certain valving and other pipe obstructions. These areas of comparative homogenization (mixing) are better suited to sampling two-phase flow.

If two-phase flow is present (usual in artesian flow), phase mixing is optimized in vertical piping where gravity does not contribute to phase separation and stratification. Where possible, an insertable sampling probe (with the sample opening facing into the flow) should be placed within the piping to provide access to the most representative sample (GLEF 1980). The fluid homogeneity at the sampling point should be evaluated by measuring the ratio of noncondensable gas (NCG) to total liquid (condensables) at a minimum of three probe positions across the piping (preferably in a vertical position if the flow is horizontal). At one probe position the sampling rate should be varied to determine the sensitivity to sampling rate; this may be significant depending on the diameter of the sampling probe. The data obtained when varying sampling rate and probe position are useful in selecting an optimal rate and position of sampling.

Typical sampling positions following full-flow wellhead separators are also shown in Figure 2.2. Most of the problems associated with nonhomogeneity are substantially less severe downstream of the separator. When practical, a probe should be used to sample even the presumedly homogeneous phases. This is important both in the steam line and in the brine line (if the pipe may be internally scaled over). Recommended sites for separated liquid or brine sampling (where probes are unavailable) are located toward the bottom of horizontally oriented pipe.

When sampling for constituents carried by droplets or particulates suspended by the gaseous flow (such as nonvolatile brine constituents), isokinetic sampling probes collect the most representative sample. Sampling should be conducted in a manner to avoid condensate traps or gravity-induced noncondensable gas/condensate separation. Sampling positions should be chosen to eliminate possibilities for sampling liquid accumulation in gaseous streams and vice-versa. Tests in steam flows have shown that probes extending into the main flow (and away from the wall where moisture films might travel) extract the most representative samples of volatiles (e.g., H_2S) in steam flows, but the sample rate (isokinetic or not) is relatively unimportant.

2.1.2 Sampling Devices

Wellhead pressures usually dictate the need for high-pressure-integrity sampling equipment. Sampling equipment must be designed to handle the anticipated stress at the sampling location. In addition, the materials selected should be chemically inert with respect to the fluid constituents. The materials of choice are usually stainless steel and Teflon®, although inconel, titanium, or another alloy may be preferable for permanent installation in concentrated brine systems in which stainless steels may undergo chloride attack. Some stainless steels have failed abruptly in these systems but not on small sampling components (to date). Be aware that after some time a Teflon lining may separate or be perforated due to mechanical factors (or thermal problems in very hot flows).

Two types of wellhead fluid sampling devices are shown in Figures 2.3 and 2.4. Brine fluids are sampled directly by an insertable probe (Figure 2.3), while brine is condensed during sampling by the sampling train shown in Figure 2.4. Both can be used for sampling wellhead fluids either before or after a wellhead separator. If the well is not pumped to maintain a single phase the preseparator (two-phase) samples may be very biased, especially with regard to volatile components. In an operating plant, cooling water flow may be available and serve the same purpose as the ice/water mixture in Figure 2.4. In this case a commercial sample condenser (Calgon Corp. or equivalent) is convenient.

To accommodate the insertable probe, an unobstructed path through the valve is necessary. Gate or ball valves usually provide this path. The inlet tip of the probe then becomes the sample point and can be positioned at the center of flow in the pipe or numerous points traversing from side to side or top to bottom within the pipe for horizontal or vertical penetrations, respectively.

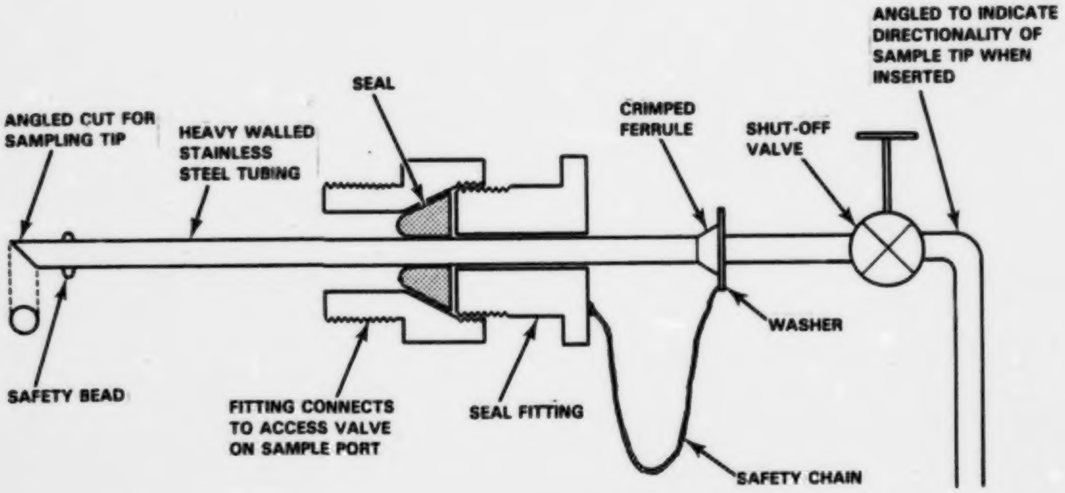

ANGLED TO INDICATE DIRECTIONALITY OF SAMPLE TIP WHEN INSERTED
SEAL
CRIMPED FERRULE
ANGLED CUT FOR SAMPLING TIP
HEAVY WALLED STAINLESS STEEL TUBING
SHUT-OFF VALVE
WASHER
SAFETY BEAD
FITTING CONNECTS TO ACCESS VALVE ON SAMPLE PORT
SEAL FITTING
SAFETY CHAIN

FIGURE 2.3. Sampling Probe

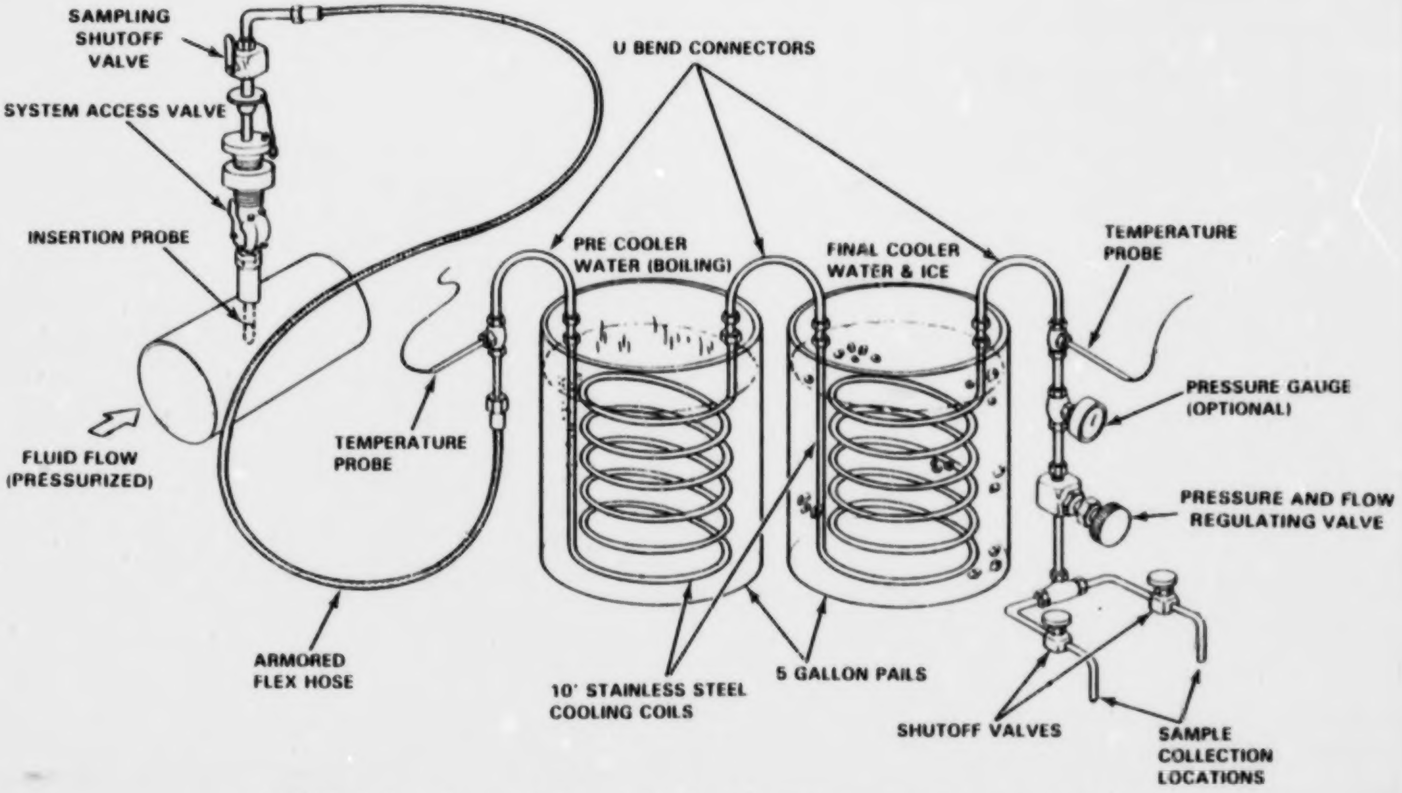

SAMPLING
SHUTOFF
VALVE
SYSTEM ACCESS VALVE
INSERTION PROBE
FLUID FLOW
(PRESSURIZED)
U BEND CONNECTORS
PRE COOLER
WATER (BOILING)
FINAL COOLER
WATER & ICE
TEMPERATURE
PROBE
TEMPERATURE
PROBE
PRESSURE GAUGE
(OPTIONAL)
PRESSURE AND FLOW
REGULATING VALVE
ARMORED
FLEX HOSE
10' STAINLESS STEEL
COOLING COILS
5 GALLON PAILS
SHUTOFF VALVES
SAMPLE
COLLECTION
LOCATIONS

FIGURE 2.4. Example Assembly (particularly suited for liquid flows)

Use of an isoenthalpic (isokinetic) pipe probe has also been proposed as an acceptable sampling technique to obtain a representative portion of the brine flow. This technique is conceptually accepted as the best of the techniques to sample two-phase brine flow for total composition; however, it is difficult to achieve in practice and is not used in favor of sampling downstream of an efficient full-flow separator. Ideally, flow velocity through the probe should be matched to the main flow to provide isokinetic sampling, a method recommended by Riley et al. 1978.

2.1.3 Sampling Procedures

Brine Fluid

The equipment for separated brine collection, shown in Figure 2.4, can be used to collect brine directly. This method is recommended for sampling, provided the sample is stabilized for the subsequent analyses. The stabilization conditions, which are described in Section 3.0, can be summarized as acidification, dilution, gas scrubbing, and filtration. The use of a low-pressure separator (rather than a scrubber) downstream of this equipment to determine noncondensable gas content has been shown to yield erratic results due to dissolution of the NCG in the cooled brine.

In certain plant locations piped cooling water may be available and used in a commercial sample condenser to replace the buckets and ice/water coolants shown in Figure 2.4. Typically, sufficient cooling is supplied to cool the brine to below 30°C, except perhaps during the summer. Construction and operation of the sample train is described in detail in Kindle and Woodruff (1981). Briefly, the valves in the Figure 2.4 assembly may be either stemmed valves or small ball or plug valves. A ball valve is best for the "sample shutoff valve" because it can be closed quickly in case of an abrupt leak. Due to corrosion problems, copper-based alloys (brass) are avoided.

To initiate and regulate flow, the following sequence is followed:

1. close all valves

2. insert probe in seal

3. open probe valve and system valve (pressurized-careful!)

4. insert probe to sampling position, tighten seal and secure safety chain

5. open ball valve of flex hose exit

6. check for system leaks in coils

7. fill buckets with water and ice

8. open one exit shut-off valve

9. open regulating valve and adjust for desired temperature on exit temperature probe.

To stop the flow, the main inlet ball valve ("sample shutoff valve") is used.

If there is a possibility of two-phase flow, follow that recommended procedure (Section 2.2). Cooling of the brine before pressure reduction prevents the formation of $CaCO_3$ scale deposits in the sampling equipment. This apparatus should be compared with a related sampling setup that is used for steam sampling/condensing (Figure 2.5).

Brine/Steam Sampling Separators

Small sampling separators (partial flow) are used to determine the amount of NCG in a brine flow if a full-flow separator is not available. One of the many designs is shown in Figure 2.6. It is commonly used during attempted sampling of two-phase brine flows and can also be used post (full-flow) separator to determine residual NCG content. A typical operation is described as follows.

Brine fluids are allowed to flow at a convenient rate from the sampling probe to the exhaust relief vent, thereby creating a constant fresh influx of brine fluids. Subsequently, the separator valves are opened slightly to allow separator flushing and thermal equilibration of the equipment. Then the relief valve is closed, along with both the steam and separated brine valves. Brine flow into the separator is controlled by the main separator valve. When brine reaches the observation level within the sight glass, both the steam flow and separated brine valves are adjusted to allow flow into samplers or other processing equipment downstream. Meanwhile, the main separator valve is adjusted to maintain the brine fluid within the observable range. Fine control of the liquid level is achieved by carefully adjusting the separator brine exit valve. In this way, a balance is established between the incoming brine fluids and the exiting separated gaseous and liquid phases. In practice this balance can be difficult to achieve in the field without constant attention.

Typically, samples of the liquid phase are collected by flowing the liquid through a cooling coil system similar to that shown in Figure 2.4 where the hot brine is cooled to ambient temperatures while under pressure. Samples of the

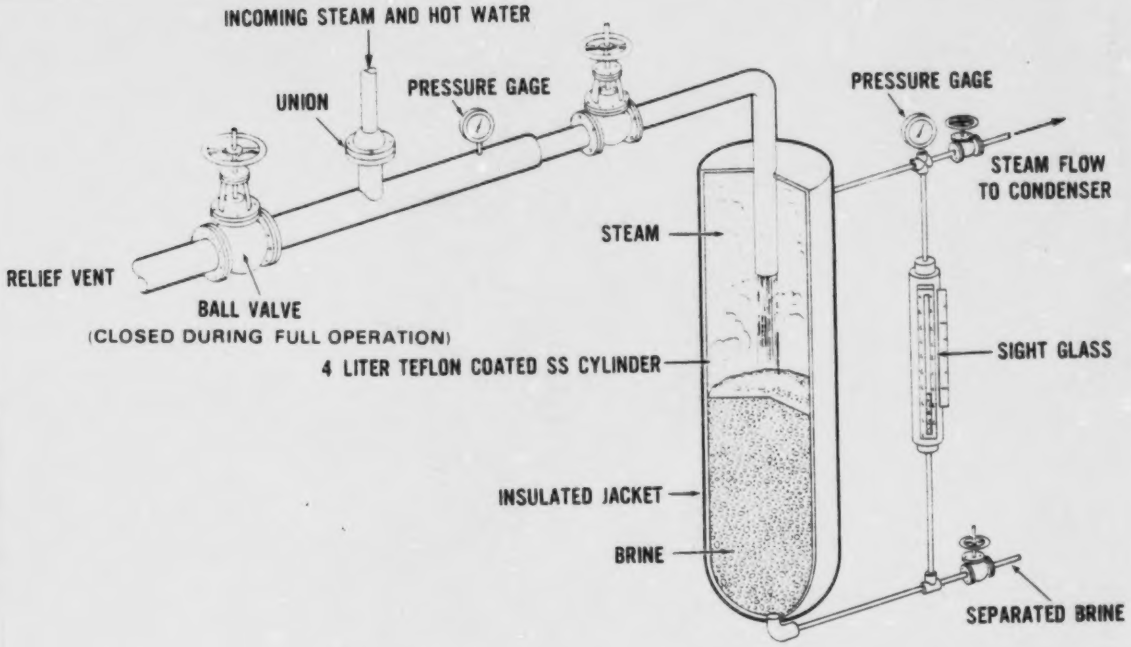

INCOMING STEAM AND HOT WATER
UNION
PRESSURE GAGE
PRESSURE GAGE
STEAM FLOW TO CONDENSER
STEAM
RELIEF VENT
BALL VALVE
(CLOSED DURING FULL OPERATION)
4 LITER TEFLON COATED SS CYLINDER
SIGHT GLASS
INSULATED JACKET
BRINE
SEPARATED BRINE

FIGURE 2.6. High-Pressure Separator

liquid may be collected in appropriate containers. Steam and gas samples are collected as described in the section on steam sampling (Section 2.4).

The main concerns to look for in the operation of this partial flow (sampling) separator are given below.

1. The fraction of NCG evolved to the gas phase may be affected by the separator pressure. This pressure should be adjusted to match the pressure of the first plant separator. If this test is being performed on a well to estimate the NCG emissions, the separator should operate at a pressure resulting in at least an 8% steam flash. This steam flash ensures that the majority of the NCG is in the gas/steam phase.

2. The NCG fraction evolved is dependent on temperature, particularly if the temperature is below boiling. The separator should be operated as close to system temperature as possible. Insulation is recommended.

3. The NCG fraction evolved may be dependent on the flow rate through the separator if either a) the temperature is low or b) the flow is being pulled from a larger two-phase flow. In these cases the flow rate should be varied to determine the sensitivity; a five- to tenfold flow variation is recommended. Sampling downstream of a full-flow separator is preferable.

2.2 SAMPLING TWO-PHASE FLOW

Geothermal fluids may be liquid or gas or a two-phase mixture of both, depending upon the type of geothermal resource and temperature-pressure conditions. The information on two-phase flow in this subsection is more detailed than for brine or brine/steam separators because of the difficulty of reliable sampling and is therefore treated separately. Particulates carried along with the fluid flow are not considered as a separate phase.

A vapor-dominated geothermal reservoir delivers steam containing some fraction of noncondensable gases. A hot liquid reservoir produces both pressurized liquid with some dissolved and free gases or a two-phase flow of steam and entrained water, if temperature and pressure conditions permit flashing.

NOTE: It is recommended that low reliability be placed on the analysis from a two-phase sample; a better analysis will come from samples collected downstream of a full-flow separator. If two-phase sampling is attempted, an indication of the possible errors can be achieved by comparing the results on a series of probe-collected samples taken at different locations within the flow, and at different sampling rates. The variations in gas-liquid ratios of these samples, which are measurable in the field, can be used to immediately perceive the variability.

2.2.1 Sample Site Selection

Sample composition can be influenced by where samples are taken from the wellhead and associated delivery system piping. Consequently, a location should be chosen to minimize changes in the fluid composition. Sampling locations upstream of piping constriction may give consistent results, while downstream samples reflect added steam that is the result of flashing due to pressure drops. Gravity can create phase separation in horizontal piping after only short runs, and representative sampling of the combined fluids is difficult. Figure 2.7 gives an indication of the variety of two-phase flow regions that occurred in one study of a brine-dominated geothermal source (Freeston and Lee 1979). The advantages of upstream sampling location in vertically oriented

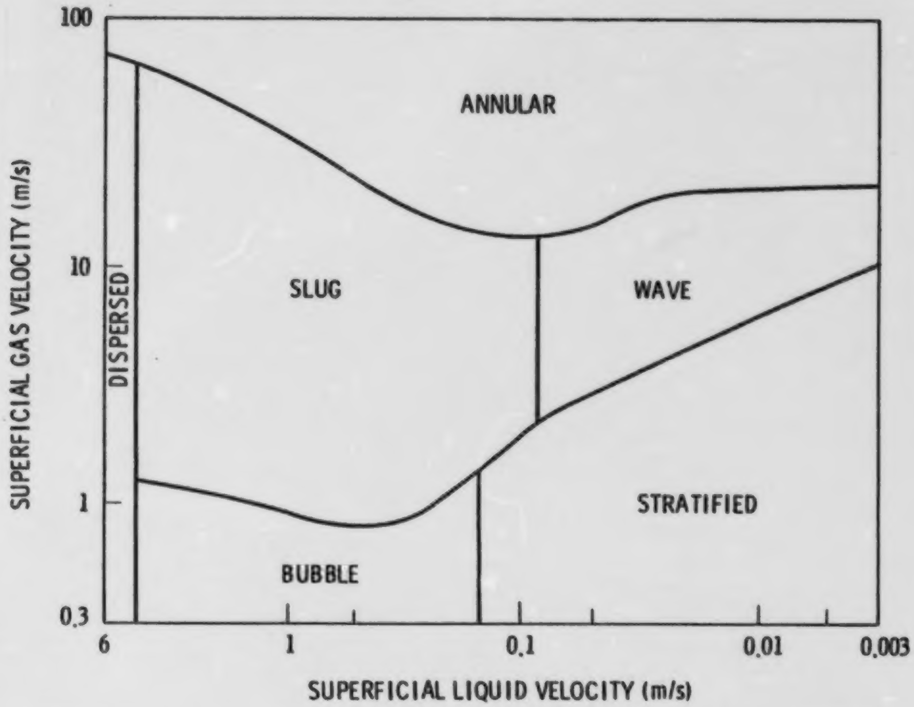


FIGURE 2.7. Two-Phase Flow Regions (Freeston and Lee 1979)

piping or in turbulent fluid flows (elbows) can be seen if two-phase sampling is attempted.

2.2.2 Sampling Design and Devices

The high-pressure separator (Figure 2.6) and a steam condenser (Figures 2.5 and 2.10, Section 2.4.2) can be used in series for separating steam and NCG from the brine so that components of both phases can be sampled.

2.2.3 Brine/Steam/NCG Ratios Procedure

The separator is flushed, and both the line pressure and temperature are re-established. Next, steam flow from the separator to the condenser is adjusted so that the operating capacity of the condenser is not exceeded. With the separated brine fluid level within the sight-glass readout range, the incoming brine and separated brine flows are adjusted to maintain the separated brine level throughout the experimental measuring process.

Steam and noncondensable gases enter the condenser where steam is condensed and the gases exhausted. The section on sampling steam lines in power plants (Section 2.4) describes the operation of the condensers. A simultaneous measurement is made of the separated brine volume (mass), the condensate water volume (mass), and the noncondensable gas volume. The level on the separator sight glass is noted and maintained during the separated brine steam NCG measurements particularly at the start and finish.

The measurements necessary to determine the brine/steam/noncondensable gas ratios for two-phase flow systems are similar to those necessary when making quantitative determinations of components in single-phase flow systems. Field measurements include:

- Brine weight or volume. The brine weight is measured in the field, if possible. Should this be impractical, the volume is measured and the sample returned to the laboratory for weighing or an aliquot is taken for density measurements. Temperature measurements are made at the time of the volume measurements for density corrections. The results are usually expressed in units of kilograms of brine.

- Steam condensate weight or volume. Again, it is preferable to weigh the condensate; however, volume and temperature measurements are adequate to determine the steam condensate weight. A density factor, taken from standard tables, converts water volume to weight. The results are usually expressed in kilograms of condensed steam.

- Noncondensable gas volume. Several corrections and calculations are needed to convert the measured gas volumes to gas volume at standard conditions.

  First, a correction to the measured volume is made because of the contribution of the vapor pressure of water to the total observed volume. The vapor pressure of water depends upon the temperature, T, at which the measurements were made. Their relationship is given in standard tables. This corrected volume, V, is calculated as follows:

$$V = V_x \frac{P - P_{H_2O}}{P}$$

  where V_x is the gas volume measured, P is the atmospheric pressure, and P_{H_2O} is the vapor pressure of water at temperature T. Secondly, the atmospheric pressure and the temperature at which the gas was measured are used to correct the gas volume to standard conditions. Typically, the temperature of the water in the wet-test meter is the temperature at which the gas was measured. The volume, V_o, at standard conditions is given as follows:

$$V_o = \left[\frac{V_x\ P\ T_o}{P_o\ T}\right]$$

where V_x is the gas volume measured and P and T are pressure and temperature at which measurements were made. V_o is the volume at the standard condition where P_o = 1 atmosphere and T_o = 273° absolute temperature.

The results are usually expressed in liters of gas volume, V_o.

NOTE: When using the NCG/brine ratios to determine the variability and sampling error during two-phase sampling in the field, it may not be necessary to apply these corrections since the ambient pressure and temperature will probably not vary during the course of the test. What is being sought is the variability of the ratio, rather than an absolute value, so it can be used to help define the best sampling rate and location within the flow.

2.3. SAMPLING BINARY CYCLE PLANTS

Binary cycle geothermal power plants do not flash the fluid into steam, but keep the water under pressure in the piping and heat exchanger loops until it is returned to the ground via injection wells. Therefore, the fluid sampling is considerably simplified, and sampling either the incoming or the injected liquid as described under Section 2.1.3 will provide adequate characterization of the hot water. These sampling points are shown in Figure 2.8. Unless some brine treatment process is incorporated, the injected fluid can be assumed to have no additional pollutants. Geothermal brines from binary cycle geothermal power plants are best sampled by using the device previously illustrated in Figure 2.4. In this system, there is no need for steam/brine separation since flashing of steam and release of volatiles to the atmosphere do not occur. A total fluid sample including gas scrubbers, therefore, is sufficient to characterize the flowing system. It is also valid to use a high-pressure separator upstream of the condensers and sample both gas and flashed brine. However, the added complexity does not yield any benefit and may result in lower Ca and CO_2 concentrations due to possible scaling in the separator.

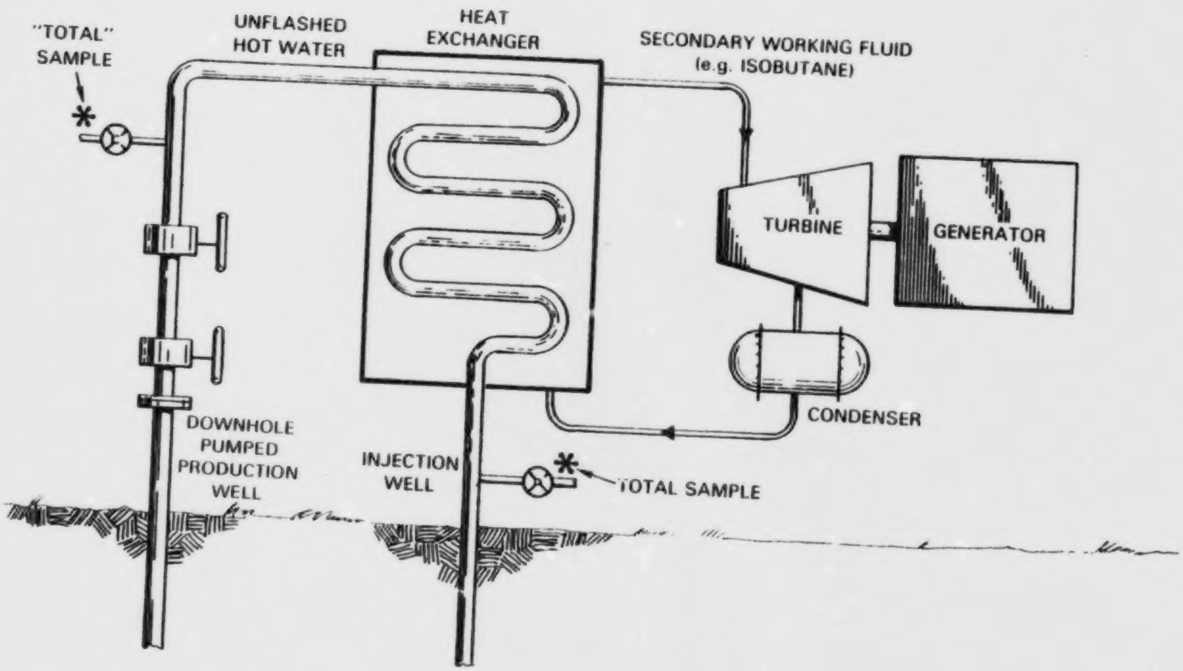

"TOTAL" SAMPLE
UNFLASHED HOT WATER
HEAT EXCHANGER
SECONDARY WORKING FLUID (e.g. ISOBUTANE)
TURBINE
GENERATOR
CONDENSER
DOWNHOLE PUMPED PRODUCTION WELL
INJECTION WELL
TOTAL SAMPLE

FIGURE 2.8. Sampling Scheme at a Binary Cycle Geothermal Power Plant

2.4 SAMPLING STEAM CYCLE PLANTS

2.4.1 Sample Site Selection

There are usually several key positions throughout dry steam or flashed steam geothermal power plants where sampling is both desirable or necessary. These positions include incoming steam lines, condenser outlets, and off-gas ejector abatement systems or comparable locations. Typical sampling sites are shown in Figure 2.9.

Steam Lines

Incoming steam lines are thermally insulated and normally have horizontally mounted valves that serve as sampling points just outside the power plant. It is generally accepted that the reasonably single-phase, steam-gas flow can be sampled in a representative manner from an upstream-facing probe inserted through these ports (valves). The isokinetic aspect of sampling (matching the sample stream velocity to the main flow velocity) for NCG determinations is relatively unimportant; however, the use of a probe extending into the main flow (rather than a common surface tap) is important. A permanently mounted probe in the steam line may become partially plugged by deposits and should be inspected and cleaned during plant maintenance periods. Sampling positions located at the bottom of the steam lines should be avoided because small amounts of condensate may collect there. Some geothermal power plants have small steam sampling condensers in place to condense and allow steam sampling for gases and condensate (Figure 2.5).

Condenser Outlets

Gas samples of spent condenser gases can be taken in the condenser exhaust piping. Special sampling lines are usually installed at these power plant piping positions to allow convenient sampling.

The spent noncondensable gases require quantification while still within the plant piping system. Alternative flow paths for these gases could include direct routing through an off-gas ejector to the environment, processing through a pollutant abatement system, or piping the gases to the cooling tower where they are dispersed in the cooling tower exhaust or possibly reinjected into the ground.

Off-gas Ejector

Gaseous samples can usually be taken from horizontal ports along the off-gas ejector stack. Sampling ports installed in the off-gas lines either horizontally or from the pipe top are preferred in order to eliminate small amounts of condensate fluids. In these locations a probe is not necessary for sample

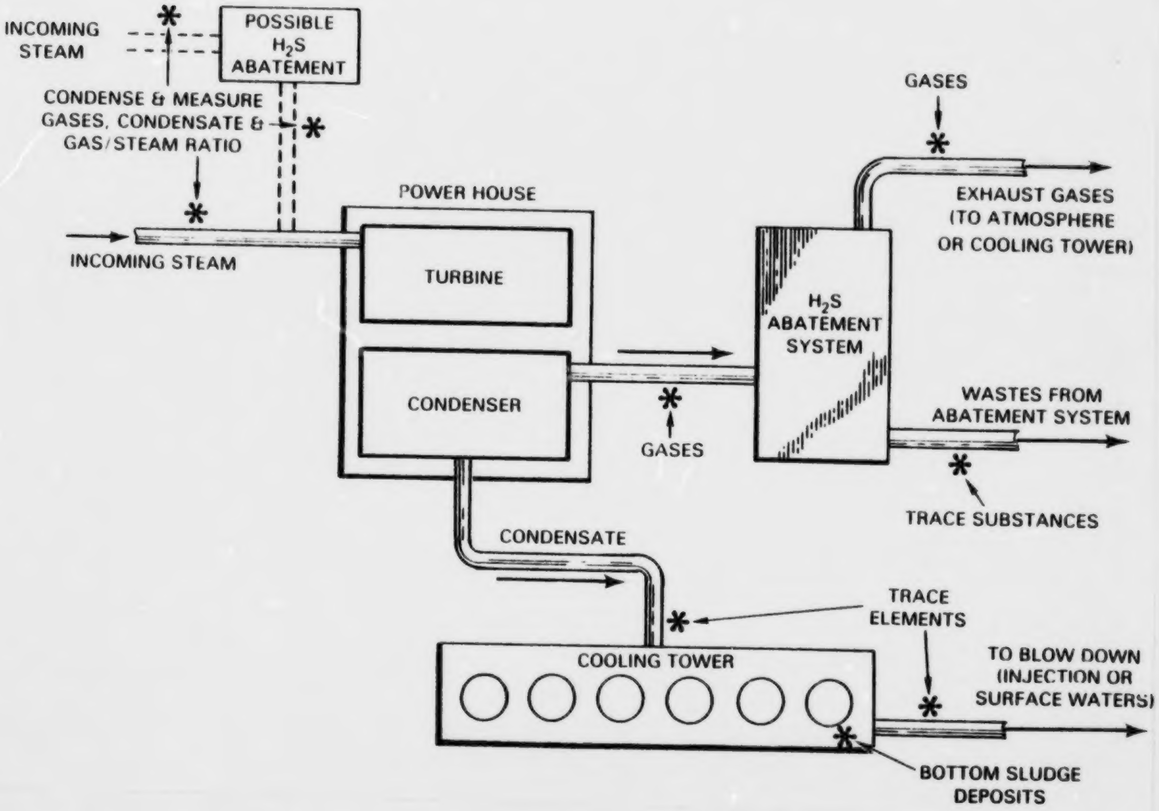

INCOMING STEAM
POSSIBLE H_2S ABATEMENT
CONDENSE & MEASURE GASES, CONDENSATE & GAS/STEAM RATIO
INCOMING STEAM
POWER HOUSE
TURBINE
CONDENSER
GASES
H_2S ABATEMENT SYSTEM
GASES
EXHAUST GASES (TO ATMOSPHERE OR COOLING TOWER)
WASTES FROM ABATEMENT SYSTEM
TRACE SUBSTANCES
CONDENSATE
TRACE ELEMENTS
COOLING TOWER
TO BLOW DOWN (INJECTION OR SURFACE WATERS)
BOTTOM SLUDGE DEPOSITS

FIGURE 2.9. Sampling Scheme at a Typical Dry Steam or Flashed Brine Geothermal Power Plant

extraction since the NCG is the major species present, whereas in the steam lines the NCG is a minor component (<1%) and more care must be taken during its sampling. This differentiation would not hold for steam-powered ejectors. Other gas sampling sites normally are located in the manifold that distributes the condenser off-gases or abatement system off-gases to the individual stacks of the cooling tower. A representative sample of these gases is taken from this manifold before the gas is distributed throughout the cooling tower. Abatement system sampling sites are chosen just prior to and immediately following the system.

Steam condensate can be sampled either immediately after exiting the condenser or as it enters the top of the cooling tower. In facilities with direct contact condensers, cooling tower water is sprayed directly on the steam as it leaves the turbine; at this point the water is a mixture of fresh condensate and cooling tower water. In facilities with surface condensers the cooling tower water flows through a heat exchanger and is not in direct contact with the steam or condensate fluid. It is important to sample the water entering the top of the cooling tower and at the bottom of the tower (blowdown) because significant losses of constituents and dissolved gases occur as the water cascades down through the cooling tower.

2.4.2 Sampling Devices

This subsection describes the devices for sampling steam lines and gas exhausts in steam cycle plants. Incoming steam from the insertion probe shown in Figure 2.3 (for steam a probe constructed to ASTM or ASME specifications is also acceptable) is condensed by one of the three types of steam condensers described: nonmetallic, steel coil, or evacuated glass.

Nonmetallic Steam Condenser

The glass apparatus (Figure 2.10) minimizes chemical interactions and prevents metallic contamination of the condensate if the very finest analyses are intended. Robertson and Ludwick (in Watson 1979) described this device. The purpose of this device is to condense steam and separate the condensed water from the noncondensable gas phase. The main condenser is a large spherical surface condenser that can handle large sample volumes (up to 10 L). These large volumes minimize errors that can occur in low volume sampling devices. A glass cooling coil surface condenser serves as a backup to assure that all condensables have been collected. Cold water is continuously pumped over the large spherical condenser and through the jacket of the small condenser. The source of this water may be a self-contained ice bath, or if available, a source of the plant tap water. This device should be (low) pressure tested and a pressure gauge and/or a transparent shield is recommended during use.

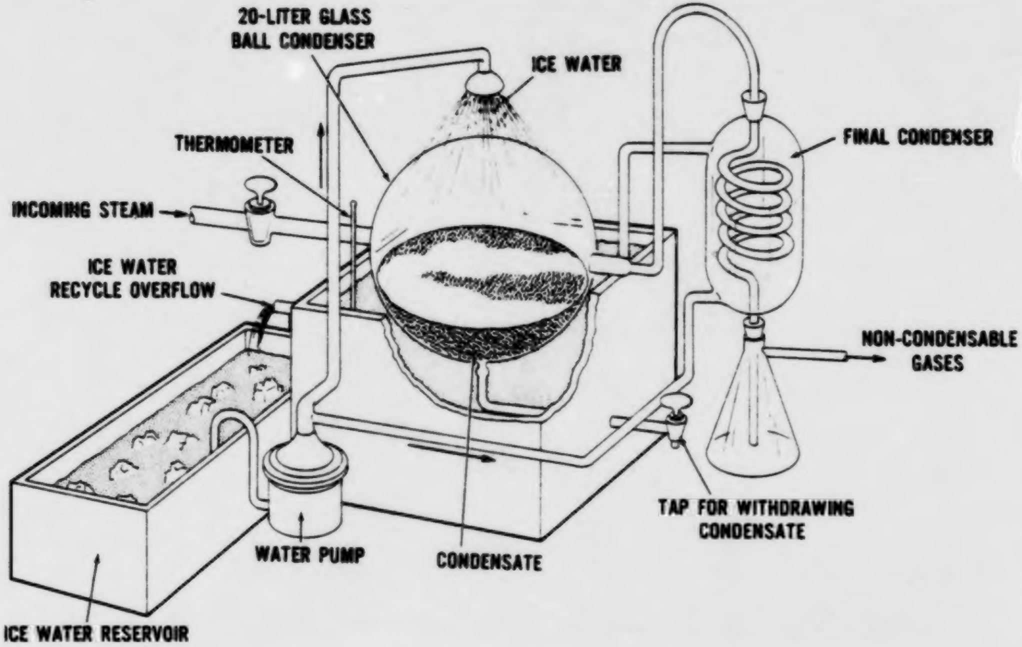

20-LITER GLASS BALL CONDENSER
ICE WATER
FINAL CONDENSER
THERMOMETER
INCOMING STEAM
ICE WATER RECYCLE OVERFLOW
NON-CONDENSABLE GASES
TAP FOR WITHDRAWING CONDENSATE
WATER PUMP
CONDENSATE
ICE WATER RESERVOIR

FIGURE 2.10. Nonmetallic Steam Condenser

Steel Coil Steam Condenser

Built-in plant piping for condensing and sampling incoming steam is usually present at each power plant (Figure 2.5). This piping includes a cold water jacket surrounding a stainless steel coil for condensing the steam. The output of this condenser is a heterogeneous mixture of noncondensable gas and steam condensate. It should be operated for several minutes prior to sample collection to ensure a steady-state operation. The sample may be collected in a scrubber, or a simplified separator system may be used to collect separate phases of the fluid (as shown in Figure 2.5). Related equipment and procedure are described by Christofferson et al. (1975).

Evacuated Glass Steam Condenser

An evacuated glass bulb containing base (NaOH, NH_4OH) may serve as a total scrubber, as described above, or as a self-contained scrubber/condenser as described in the steam sampling procedure. Ellis and Mahon (1977) and Nehring and Truesdell (1977) described such an apparatus. Using the bulb is not as suitable for determining radon concentration as the other techniques where a large volume sample of NCG may be collected with very little condensate.

Off-Gas Ejector Sample Devices

For sampling gas exhausts from an off-gas ejector, horizontally oriented sampling ports are utilized to obtain representative samples of the separated noncondensable gas fraction of the geothermal fluids. These systems are usually under a positive pressure of about 10 to 20 psig. Pre-evacuated inert sampling containers (0.5 to 2 l volume) made of Teflon, stainless steel, glass, or plastic may be used as the sampling device, depending on compatibility with the constituent(s) being measured. Hydrogen sulfide gas of geothermal origin, for example, can be stored for only short periods of time in stainless steel containers (even if Teflon-lined) because of apparent reactions with the metal, possibly in the valve. Plastic-aluminum-plastic sandwich construction sampling bags are also acceptable if they are flushed repeatedly to obtain a pure sample. Clear plastic sampling bags are not acceptable (Soinski 1977).

Scrubbers or gas sampling trains frequently are used for sampling the noncondensable gases. Where the line pressure is sufficient, the gases may be passed directly through rotometer or integrating type flow meters to determine the volume of gas sampled before the gas enters the scrubber or sampling train. Where insufficient line pressure is available, an inline pump must be installed. If the pump internals are made of completely inert materials, the pump can be placed at the upstream end of the sampling train; if not, the pump must act as an air exhaust.

2.4.3 Steam Cycle Plant Sampling Procedures

Once the steam is extracted via a probe three ways can be used to condense the steam so that the constituents can be determined:

- spherical nonmetallic condenser method
- steel coil condenser method
- evacuated glass condenser method.

If radon content is of concern the analyst will find it easier to work with a large gas sample such as would come from either of the first two methods. If a sample probe is not available and a sample is pulled directly from a surface-mounted valve (not recommended), the advantage would clearly seem to be with those methods that could handle a large flow of steam. This is based on the assumption that when sampling from a position of possible nonrepresentative composition (the wall), it is good to pull a large flow which would have to be drawn over a larger area. As described here, the first and last methods can handle large flows, but there is no reason why larger coil condensers could not be constructed and utilized. Beyond these two concerns, these methods will probably give comparable results when used as described. A direct comparative test has not been done.

A fundamental problem occurs when sampling steam to determine NCG content: in the steam line both the NCG and the water are in the vapor state; after the condensation the water is a liquid, but the NCG is present as both free gas and dissolved gas in the condensate. Unless a scrubber bottle is used to trap the NCG, it is important to perform the sampling to minimize the amount of dissolved NCG. The pH of steam condensates is variable and can dramatically affect the solubility of NCG. Acid gases, CO_2 and H_2S, make up the bulk of NCG and will dissolve readily in water unless it is acidic. NH_3 is generally soluble in water and will not readily stay in a gas phase over water. Because all gases dissolve in water in proportion to the applied pressure, the first two methods use a low-pressure condenser. The evacuated glass condenser method does not attempt to separate the NCG from the condensate.

An excellent but very specialized method exists for the real-time determination (monitoring) of H_2S in steam or NCG pipelines by adapting ambient monitoring equipment to handle the higher concentrations. This method is described in the analytical methods section (Section 4.0, method 4.4.6).

Spherical Condenser Methods

The apparatus illustrated in Figure 2.10 is used to obtain samples from incoming steam lines at geothermal power plant locations. Starting the water pump provides cold water flow onto the condenser top and through the secondary condenser. The incoming steam line control valve is slowly opened, and steam condensation begins. The condensate and gas sampling taps on the apparatus are initially open to allow system flushing. The condensate tap is then closed, and a pressure-regulating rotameter is connected to the noncondensable gas outlet. Scrubbers, sampling trains, or other special gas sampling devices can also be connected to the outlet of the pressure-regulating rotameter for sampling the noncondensable gases. By keeping the gas phase in the main condenser pressurized to approximately 5 psig, a steady flow of noncondensable gas can be maintained through the flowmeters, thereby allowing accurate measurements of this sampled gas volume. The inlet control valve is adjusted to provide the operating pressure (2 to 8 psig) within the condenser. Condensate accumulates in the bottom of the condenser cylinder while noncondensable gas starts displacing air above the condensate. The condenser is rinsed by the condensate and initial volumes are discarded. The condensate liquid level is kept high in the spherical condenser to minimize gas volume and the noncondensable gas sparging time.

About 30 min of operation are required before representative gaseous sampling can take place. Once the system is stabilized, however, very large aliquots, representative of the incoming steam, are available for continuous sampling. The temperature of the water bath serving the glass ball condenser is monitored and maintained constant by regulating the spray flow over the condenser and the ice content of the circulating water reservoir. Maintaining a constant temperature is necessary to prevent volume fluctuations due to gas temperature changes.

Liquid samples (steam condensate) are collected directly by periodically draining portions of the condensate. Gaseous samples are typically collected in evacuated containers with inlet and exit valves. The containers are connected to the condenser gas exhaust line by using standard techniques for flushing the interconnecting line. The inlet valve is then opened, and the container pressurized to condenser operating pressure with noncondensable gas. The exit valve is opened to allow gas flushing. The exit valve is then closed, and the sampling container is again pressurized. The entrance valve is closed, and the sample is disconnected from the system.

Steel Coil Condenser

The device shown in Figure 2.5 (repeated in this Section for convenience to reader) can also be applied for incoming steam sampling. The stainless steel condenser coil receiving the incoming steam is immersed in a large water cooling bath or else a commercial condenser is used. The condensation route must be made continuously downhill to minimize the possibility for gas bypass or liquid displacement of gas pockets. If this is not possible and the sample equipment resembles Figure 2.4 (with its upward flow) more than Figure 2.5, the tubing should be of small diameter (1/8 in. O.D.) to prevent NCG-condensate segregation. The rate of water flow through the jacket is controlled to provide condensation of the steam up to the cooling capacity of the sampling condenser. If steam persists at the sample collection point, a slower sampling rate is necessary. When possible, a control valve at the condenser inlet position is used to allow the condenser to operate at ambient pressure and thus minimize gaseous dissolution in the condensate phase. Condensate and gas samples are available at the condenser exit.

Basically two ways to quantify the gas samples are usable:

- A simplified liquid/gas separator, such as the modified filtering flask (condensate collection bottle) shown in Figure 2.5, may be used to collect samples of the condensate while gas bulbs or bags are used for the gas phase. A small amount of HCl or H_2SO_4 can be added to the collection bottle at the start to ensure that the acid gases (H_2S, CO_2) pass through. The volume of NCG can be determined by a wet-test meter, a soap-film bubbleometer or by water displacement if care is taken to minimize NCG dissolution. The condensate is determined by weight change and is analyzed for NH_3 and boron. The other NCG components are determined from a gas bulb (or bag) sample as shown in Figure 2.5 or from a scrubber bottle (see Section 3.0).

- The NCG/condensate stream can also be quantified through flowing directly into scrubber bottles (Section 3.0 describes the scrubber solutions) and determining the condensate by weight change. Inert gases cannot be determined using this technique since the gases will not remain in the scrubber bottle.

Evacuated Glass Condenser

Another steam sampling/condenser arrangement is to collect the condensate in a pre-evacuated glass bulb that contains deaerated base, either NH_4OH or NaOH. The acid gases, H_2S and CO_2, are absorbed in the base (the others remain in the headspace and can be extracted via syringe/septum) as is the steam condensate. The collection can be made by either condensing the steam in the bulb or using the bulb to accept a precondensed steam/NCG mixture.

- Condensing in the bulb. The insulated steam sampling line ends in a "tee" with one side going to the atmosphere and the other going to the evacuated bulb located in an ice bath (Figure 2.11). The line to atmosphere is flushed until temperature equilibrium is achieved (the exiting steam must be dry and slightly bluish in color ensuring a

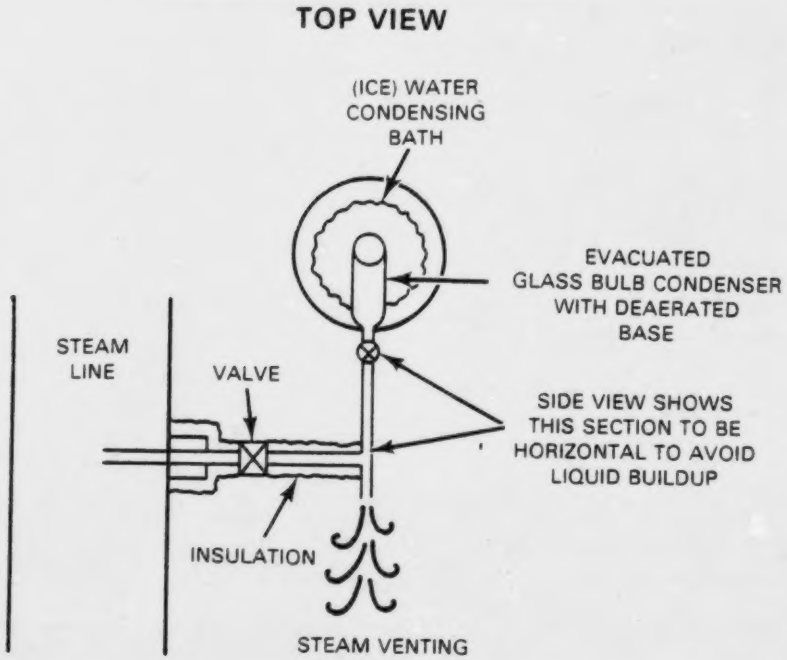

TOP VIEW
(ICE) WATER CONDENSING BATH
EVACUATED GLASS BULB CONDENSER WITH DEAERATED BASE
STEAM LINE
VALVE
SIDE VIEW SHOWS THIS SECTION TO BE HORIZONTAL TO AVOID LIQUID BUILDUP
INSULATION
STEAM VENTING

FIGURE 2.11. Steam Sampling - Evacuated Glass Condenser

single phase), then the bulb valve is slowly opened and a portion of the steam is drawn where it is condensed. When the liquid level in the bulb increases at 10 to 20% of the initial rate the sampling is completed.

- Post condenser collection. A similar "tee" arrangement is located downstream of a condenser; a separate ice bath may not be needed. In this application the evacuated glass condenser is in the position of the condensate collection bottle in Figure 2.5. The sample is collected by establishing a steady stream out of the condenser, closing the atmospheric escape completely, and slowly taking the flow into the bulb. The pressure should be monitored for safety. In this application the NCG/condensate mixture must travel through without liquid holdup in the low points of the tubing. See the earlier discussion of this point under "Steel Coil Condenser."

This method requires presampling preparation by evacuating the bulb and deaerating the base (NaOH) to eliminate oxygen which would destroy (oxidize) the sulfide. This oxygen elimination involves vacuum pumping while either gently boiling the base or putting it through a minimum of two freeze/thaw/agitate cycles. The quantity of steam collected is determined by the weight increase; the sulfide is determined by titration (using an electrode end point, Denver Research Institute 1981) or by H_2O_2 oxidation to $SO_4^=$ (and determination as $BaSO_4$ by gravimetry or turbidity).

2.4.4 Gas Exhaust Sampling Procedures

Emissions in the form of gases or aerosols are vented to the environment from a number of power plant locations and from piping associated with power plant operation. Most are planned emissions from controlled sources or from pollutant abatement systems; however, a few minor uncontrolled leaks are usually associated with geothermal energy development. This section describes controlled atmospheric emissions; quantifying uncontrolled leaks is detailed in Section 2.7.

Gas samples from off-gas ejectors or other pressurized gaseous exhaust lines are readily available for collection. Sample collection is accomplished by connecting a pre-evacuated container directly to the sampling port. Standard techniques are used for flushing the interconnecting line with the pressurized sample gas. The entrance valve on the container is opened to allow gas to fill and pressurize the container to the inline conditions. The exit line is then opened and flushing continued to eliminate air contamination from container leakage or incomplete evacuation. The exit valve is closed to allow noncondensable gas pressure to again build to inline pressure. The entrance is then closed. Any possible outward leakage of the collected sample will not affect subsequent analysis.

Unpressurized lines are sampled with a pump located to pull the gas flow through the gas sample container before it reaches the pump (being sure to allow for adequate flushing). If the pump is located before the sample container, the pump must be constructed of inert materials (such as a stainless steel/Teflon diaphragm pump) to prevent contamination or sample loss. In this case a venting "tee" is installed at the pump exhaust and before the sample vessel to allow adequate pump flushing before a sample is collected. Venting also prevents premature shutdown of many pumps due to overpressure.

2.5 SAMPLING COOLING TOWERS

2.5.1 Sample Site Selection

Gases and Drift

A composite outline of the sampling sites and the measurements necessary to evaluate operations relating to cooling tower emissions is given in Figure 2.12. The sample site locations are at the header pipes coming into the cooling tower and at individual cooling tower stacks. In some cases, samples from each of the stacks will be required. The number of cooling tower stacks at each geothermal power plant location varies from about 2 to 12, depending on their cooling capacity and the thermal requirements of the plant. In general, cooling tower stacks contain a number of ports within reach from which samples may be withdrawn by personnel on the cooling tower platform. A large single port, through which sizable probes and instrumentation may be inserted, is also conveniently located about 1 to 1.5 m above the fan blades. This position usually corresponds to a narrowing diameter section of the stack. The tower may also have a number of smaller portholes through which probes of approximately 10 mm diameter may be inserted. Typically six to seven holes are spaced equidistantly around the stack and located about 2 m above the fan blades. These holes are within easy access from the tower platform.

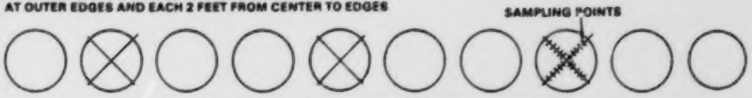
A prime sampling site is located just above the top of each stack in the exhaust plume. Here a quantitative estimate may be derived, by careful measurement, of many of the stack parameters and chemical emissions. The optimum sampling locations are level with the stack top along two 90° transits across the stack diameter. These locations, which traverse the stack, are also shown in Figure 2.12.

SELECT REPRESENTATIVE STACKS
- DRIFT PATTERN ANALYSIS
- H_2S PROBE PROFILE - PROCESS CONTROL REFERENCE POINTS†

SAMPLING ALIQUOT
- 30% OF STACKS

SAMPLING LOCATION

NOT OVER 12" ABOVE STACK TOP.
ALONG TWO 90° TRANSITS ACROSS STACK
ORIENTED 45° TO STACK CENTERLINE DIRECTION.
AT OUTER EDGES AND EACH 2 FEET FROM CENTER TO EDGES



TYPICAL SAMPLING TRANSITS: TOP VIEW OF COOLING TOWER EXHAUST STACKS

SAMPLING CONDITIONS

NO PRECIPITATION
WINDS ≦ 8 MPH
STACK FLOW RATE ≧ 90% OF DESIGN BASIS

MEASUREMENTS

PHYSICAL PARAMETERS
- MONITOR
  - FLOW VELOCITY - VANE ANEMOMETER
  - RELATIVE HUMIDITY/TEMPERATURE - WET/DRY BULB
- SAMPLE
  - PRESSURE - MERCURY BAROMETER
  - DRIFT DROP SIZE - LASER BEAM
    - DRIFT DROP PAPER PATTERN
  - INTERNAL STACK DIAMETER

CHEMICAL PARAMETERS
- TEFLON PROBE AND PUMP
- SAMPLING RATE: TO MATCH MEASURED FLOW VELOCITY
- GASES
  - H_2S - POTENTIOMETRIC MONITORING
    - AQUEOUS SCRUBBING FOLLOWED BY WET CHEMICAL ANALYSIS*
  - NH_3 - POTENTIOMETRIC MONITORING
    AQUEOUS SCRUBBING FOLLOWED BY AMMONIA ELECTRODE ANALYSIS*
    ION CHROMATOGRAPHY
  - Rn - GRAB SAMPLE IN LUCAS TUBES FOLLOWED BY α-PARTICLE MEASUREMENT
  - Hg - GOLD COATED BEAD COLUMN TRAP FOLLOWED BY AA ANALYSIS
- DRIFT
  - B - HEATED BEAD TRAP - PLASMA EMISSION
    - H_2O METHINE/COLORIMETRIC
  - F - HEATED BEAD TRAP-F ELECTRODE
    - COLORIMETRIC - SPADNS - ZrF_6 dye.
    - ION CHROMATOGRAPHY

ALTERNATE GAS METHOD

SAMPLING LOCATION

CONDENSER OFF-GAS LINE

MEASUREMENTS

PHYSICAL PARAMETERS
- PROFILE FLOW VELOCITY ACROSS OFF-GAS PIPE LINE TO COOLING TOWERS - TURINE FLOWMETER
- INTERNAL PIPE DIAMETER - ENGINEERING SPECIFICATIONS
- TEMPERATURE - PT RTD
- PRESSURE - PRESSURE/VACUUM GAGE CERTIFIED TO ≤ 0.5% ACCURACY

CHEMICAL PARAMETERS
- H_2S
  - Ag_2S ELECTRODE/TITRATION BASIC
  - IODOMETRIC TUT-WYLER/TITRATION ACID
  - ZnAc/ZnS/I/TITRATION ACID
  - GAS CHROMATOGRAPHY
  - VOLUMETRIC DILUTION - POTENTIOMETRIC
    - LEAD ACETATE PAPER
- ^{222}Rn - LUCAS TUBE/α PARTICLE ANALYSIS
- Hg - Au BEAD COLUMN TRAP COLD VAPOR AA ANALYSIS
- CO_2
  - MASS SPECTROSCOPY
  - INFRA RED
  - GAS CHROMATOGRAPHY/THERMAL CONDUCTIVITY
  - CARBONATE PRECIPITATION
- H_2 - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- N_2 - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- O_2 - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- Ar - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- CH_4 - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- C_2H_6 - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- C_3H_8 - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- BUTANES - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- BENZENE - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS
- OTHER HYDROCARBONS - GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS

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*TURBULENT GAS MIXING ACTION IN THE STACK AIR STREAM NECESSITATES FAST RESPONSE TIME INSTRUMENTAL ANALYSIS, OR GRAB SAMPLING TECHNIQUES IN ORDER TO DERIVE CHEMICAL RESULTS WHICH CORRELATE WITH THE PHYSICAL PARAMETERS BEING MEASURED.

†IT IS ANTICIPATED THAT ONCE THE EXTENSIVE STACK ANALYSES DESCRIBED ARE COMPLETED CONTINUOUS REPETITION IS UNNECESSARY UNLESS OPERATING CONDITIONS CHANGE SUFICIENTLY TO WARRANT ADDITIONAL ANALYSES. TO MONITOR OPERATING CONDITIONS, PROCESS CONTROL REFERENCE POINTS WILL BE UTILIZED TO MAINTAIN A WATCH ON THE CONTINUING ENVIRONMENTAL IMPACT OF THE COOLING TOWERS. THESE ARE SMALL, EYE-LEVEL, PORTS IN THE STACK THROUGH WHICH A PROFILE OF THE H_2S CONCENTRATION MAY BE QUICKLY DETERMINED USING A PROFILE POTENTIOMETRIC INSTRUMENT ATTACHED TO A STAINLESS-STEEL PROBE. THE RELATIONSHIP BETWEEN THE TOTAL STACK EMISSION PARAMETERS AND THIS ABBREVIATED PROFILE WILL BE USED TO ESTIMATE THE DAY TO DAY STACK EMISSIONS.

FIGURE 2.12. Cooling Tower Gas and Drift: Measurement and Analysis

Water

The water entering the cooling tower at a steam power plant using a direct contact condenser will be a mixture of fresh steam condensate and cooling tower water used at the condenser. This water is enriched in volatile substances and dissolved gases compared with the water exiting the cooling tower. Therefore, it is necessary to collect and analyze both the incoming and exiting cooling tower water. The optimum location for collecting the tower inlet water is from a tap on the main header line going to the top of the tower or from the manifold line dispersing the water at the top of the tower. Water from the bottom of the cooling tower can be sampled directly.

2.5.2 Sampling Devices

The physical or chemical parameter undergoing measurement will dictate the type of sampling design or device needed. These parameters and devices are described below.

Gas Sampling Probes

Both rigid stainless steel and heavy-duty Teflon tubing can be extended through probe holes into the cooling tower stack region of interest for sampling the gases. A glass or plastic drift collection trap, such as a modified filtering flask, can be used to remove entrained moisture from the gas samples.

Probe Supports

Physical supports are needed when measurements involving several pieces of instrumentation are to be made at locations beyond about 1 m from the stack edge. These supports can vary from a simple aluminum tube (50 mm diameter), which is inserted into the large port, to a sophisticated rail carriage structure, which supports equipment and allows its positioning above the stack top. A commercially available rail carriage is satisfactory (ESC Co., Knoxville, Tennessee, or other manufacturers).

Flow Velocity Device

A vane anemometer is used to measure the speed of the exhaust air as it flows through or out of the cooling tower stack.

Internal Stack Diameter

The internal stack diameter is determined with a tape measure. Construction engineering diagrams are also useful when other methods are not practical.

Temperature and Relative Humidity

Dry-bulb temperature is accurately measured with a platinum resistive temperature device (RTD) having an electronic instrumental readout. The temperature probe is stainless steel, and the lead wires are Teflon coated. Relative humidity is calculated from the temperature depression between the dry-bulb and a second temperature probe having the sensing zone covered with a wet wick. A drift shield is necessary to prevent moisture from impacting the dry-bulb sensor. Evaporation of the moisture would result in erroneous, lower temperatures for the dry-bulb.

Pressure

The absolute atmospheric pressure is affected by the power plant site elevation and the unique daily barometric fluctuations. A mercury manometer accurately measures this parameter.

Drift

The size of the drift droplets and the aerosols they create are necessary measurements for environmental assessment purposes. Drift size is measured with a laser beam, light-scattering technique. Alternatively, the drift droplet pattern produced on special paper can be used. Drift sampling for entrained materials is accomplished by using a heated, isokinetic flow-through impact collector (Figure 2.13).

2.5.3 Sampling Procedure

Before stack sampling can proceed, the following criteria must be met: 1) no precipitation is occurring; 2) winds are $\leq$13 km/h; and 3) the stack flow rate is between 90 and 100% of design basis.

To measure gaseous emissions from cooling towers, it is recommended that all tower stacks undergo velocity-pollutant concentration profiling if the source of the pollutant (i.e., a manifold delivering NCG) might not cause uniform dispersion. For quantitative estimates of drift from the cooling towers, only 30% of the tower stacks need to undergo velocity-drift analyses because of the greater likelihood for uniformity.

For drift analysis criteria, the stacks to be sampled in a typical 10-stack cooling tower should be selected by the following criteria: A visual examination of the drift pattern on the tower platform is made. All stacks are categorized into three groups: many large droplets, many small droplets, and few droplets. One of each type is chosen to represent all other similar drift-producing stacks. Results from each of these types are multiplied by the number of stacks in each type to derive an estimate of overall drift production.

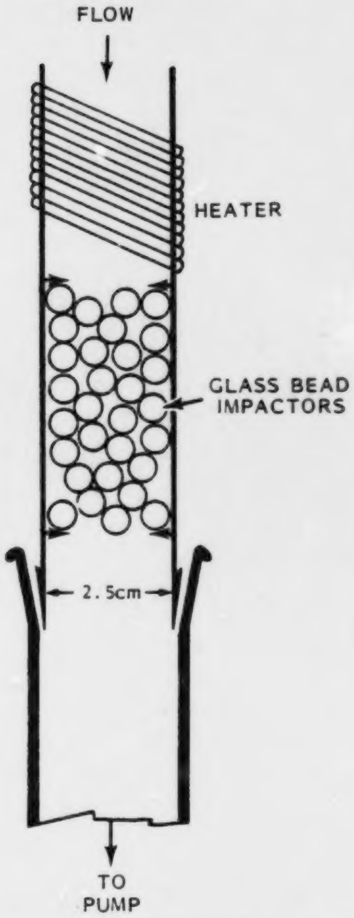

FIGURE 2.13. Flow-through Impact Collector

A measurement program is initiated for both physical and chemical parameters concurrently. A series of measurements are made to determine volumetric flow rate, pollutant concentration, and drift measurements, if necessary, at each of the sampling locations described. A pump and Teflon probe apparatus with drift trap is operated to provide stack gas samples for monitoring, collecting, and scrubbing operations for chemical pollutant analysis. At the same time, the instantaneous flow velocity and relative humidity (RH) measurements are made along with a strip chart record of all monitored variables (temperature, RH, flow velocity, H_2S concentration, and laser beam drift size distribution). Turbulent gas-mixing action in the stack gas-stream necessitates fast response time instrumental analysis or rapid grab sampling techniques in order to derive chemical results that correlate with the physical parameters being measured. Once a series (4-8) of these necessary short term measurements are completed (over a period of 24-48 hrs), then sufficient information is available to characterize the system.

Additional future sampling is warranted only when major operating parameters change or when plant monitoring information indicates that pollutants in incoming fluids or plant effluents are significantly different ($\geq$30%) than those observed during the original characterization study.

Thereafter, estimates of cooling tower emissions are derived from measurements made more conveniently at the process control ports (previously discussed), which are utilized as reference monitoring locations. A profile of H_2S concentration at each port is quickly made with a rigid stainless steel, 2-m long probe connected to a portable potentiometric H_2S monitor. The H_2S concentrations observed are related to those obtained during the full-scale stack analyses to obtain an estimate of current stack emissions.

2.6 SAMPLING AMBIENT GASES

Environmental measurements of gaseous emissions from areas of geothermal development are particularly associated with the H_2S and its products. Although this material is considered the most important atmospheric pollutant from geothermal sources, other gaseous materials such as radon and mercury may also be of environmental interest and concern.

2.6.1 Sample Site Selection

Varying meteorological and topographical parameters influence the selection of specific sites for environmental sampling and monitoring of gaseous pollutants emanating from areas of geothermal development. Usually a number of sampling sites are necessary to derive definitive ambient measurements. As the primary criterion, the protection of the public health determines the site locations. Pollutant measurements must be made in general personnel use areas and along access roads near the source. These measurements are appropriate during periods favoring atmospheric transport from the source.

In order to relate the observed pollutant concentration to the geothermal source, sufficient upwind measurements must be conducted to define the already existing atmospheric background levels of the pollutants under study. These background measurements must be taken over a time frame that is sufficiently long enough to define the daily or seasonal background fluctuations.

Another criterion for site selection is the presence of meteorological or topographical features that separately or in combination minimize dilution, thereby contributing to higher than usual pollutant concentrations. These conditions are observed in valleys where air drainage patterns constrain dispersion of pollutants. Atmospheric stability, particularly that associated with strong temperature inversions, creates much higher than usual pollutant concentration in areas that are prone to such atmospheric conditions. In general, this discussion points to measurement site locations at low elevations in all quadrants near the source, as well as some distance away in the direction of the normal wind patterns.

Finally, measurements must be made of the general, low-level pollutant concentrations as downwind travel takes place. These measurements are useful to verify conformance with air quality standards and to compare with atmospheric transport model predictions for pollutant concentration at the location under study. For rough terrain environments such as The Geysers, measurements are appropriate along ridge lines during periods of neutral stability and normal air mass movement. At less rugged locations, normal downwind pollutant concentration measurements are desirable until increased diffusion, with distance, dilutes the pollutant concentration below the sensitivity of the appropriate instrument or until dilution produces pollutant levels indistinguishable from normal background concentrations.

2.6.2 Sampling Devices

Often the atmospheric pollutant and its concentration dictate the type of sampling or monitoring device used to continually measure these materials. Moderate to low levels of H_2S can be instrumentally monitored by a flame ionization detector connected to a Teflon probe inlet line. This instrument can also be used for measurements of moderate to low levels of SO_2, an end product of H_2S air oxidation.

Several situations require the collection and concentration of the gaseous pollutants in scrubbing solutions. A typical scrubber-impinger arrangement (McCurdy and Altshuler 1977) is illustrated in Figure 2.14. Unattended, sequentially timed sample collector devices are available to time integrate the collection period. These devices are usually turntables that move the pumping position to different sampling lines.

Environmental samples may be required that reflect the time-integrated atmospheric concentration for 8 h or more. Radon gas samples are often collected in pre-evacuated glass or stainless steel cylinders, or directly into an alpha particle counting chamber such as a Lucas counter. A time-integrated sample can be obtained through a controlled gas bleed device that uses a flow orifice. A Lucas counter is shown in Figure 2.15.

Samples for mercury analysis are collected on a specially prepared column of coated quartz beads typically packed in a 4 mm ID glass or quartz tube. Various chemical forms of mercury are distinguished by differential absorption

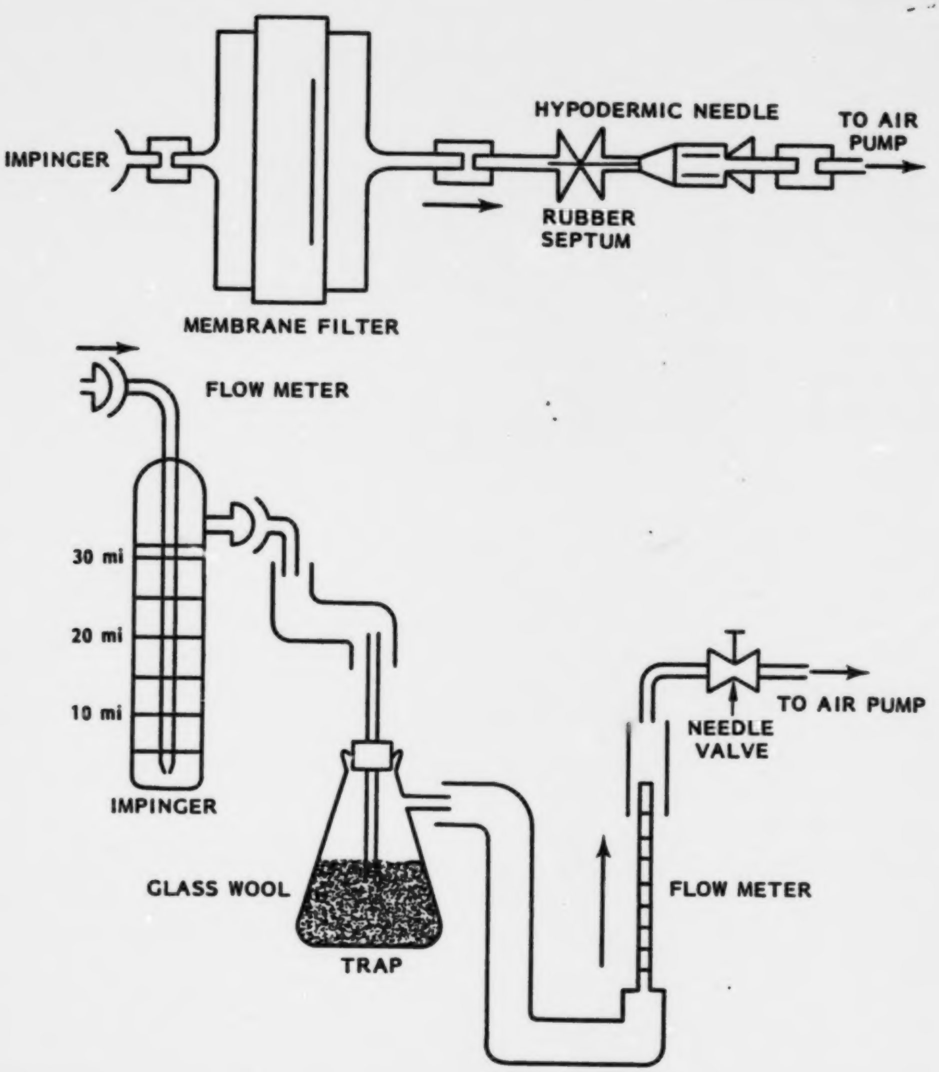
IMPINGER
MEMBRANE FILTER
HYPODERMIC NEEDLE
TO AIR PUMP
RUBBER SEPTUM
FLOW METER
30 ml
20 ml
10 ml
IMPINGER
GLASS WOOL
TRAP
NEEDLE VALVE
TO AIR PUMP
FLOW METER

FIGURE 2.14. SO_2 Sampling Train

on beads that contain different coating materials, or mercury can be collected nonselectively using only gold-coated beads. Figure 2.16 illustrates the design of the sampler (Braman and Johnson 1974, Robertson et al. 1977).

The dynamic method of sampling environmental pollutants is applicable to geothermal pollutants. A mobile laboratory or simply a vehicle able to

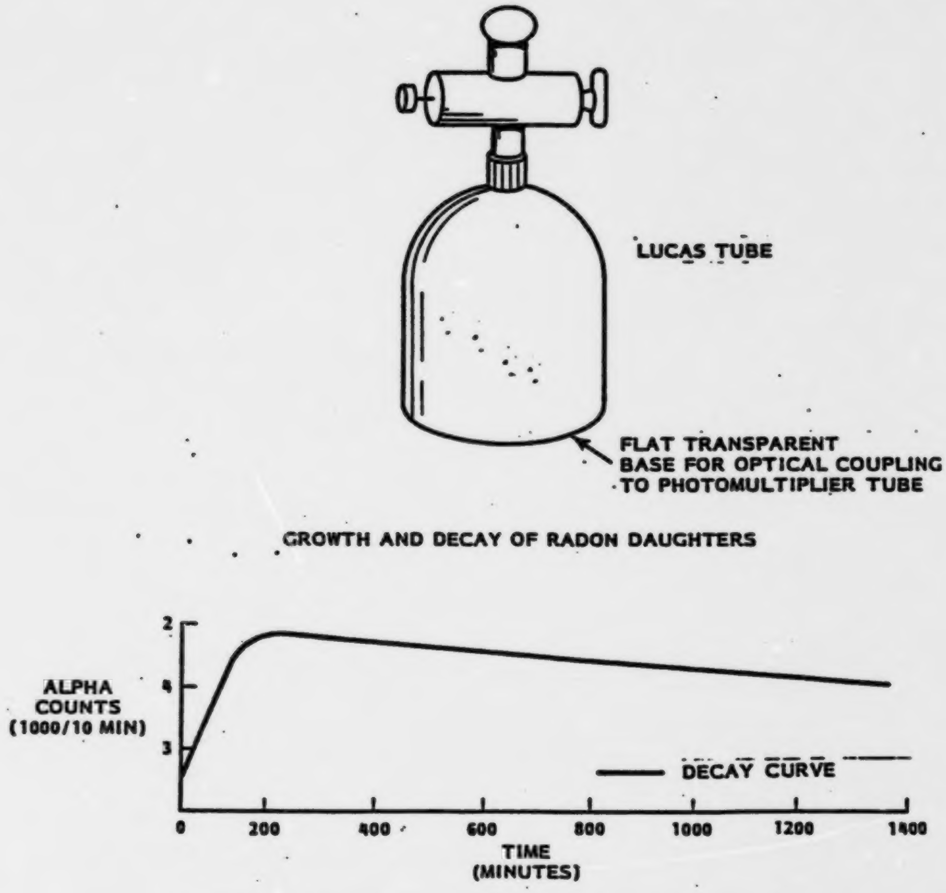
LUCAS TUBE
FLAT TRANSPARENT BASE FOR OPTICAL COUPLING TO PHOTOMULTIPLIER TUBE
GROWTH AND DECAY OF RADON DAUGHTERS
ALPHA COUNTS (1000/10 MIN)
2
4
3
DECAY CURVE
0
200
400
600
800
1000
1200
1400
TIME (MINUTES)

FIGURE 2.15. Lucas Tube and Radon Decay Curve

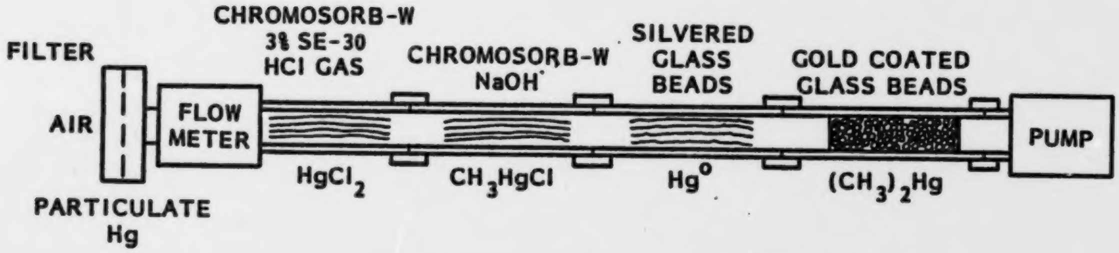
FILTER
AIR
PARTICULATE Hg
FLOW METER
CHROMOSORB-W 3% SE-30 HCl GAS
HgCl2
CHROMOSORB-W NaOH
CH3HgCl
SILVERED GLASS BEADS
Hg0
GOLD COATED GLASS BEADS
(CH3)2Hg
PUMP

FIGURE 2.16. Selective Absorption Tubes for Mercury Forms in Gases

transport and supply power to instrumentation can be used to make ambient air concentration measurements. This method can monitor or sample over a wide area and, therefore, replace an expensive stationary monitoring or sampling network.

In addition, it is very useful to be able to move the measuring equipment to the position of the effluent plume. Using the mobile approach, results are obtained for pollutant concentrations in a minimum of trials. Because of the dynamic nature of the measurements, it is possible to map the distribution of the air pollution in both space and time. With these direct measurements, estimates of air quality are unnecessary and conformance to Air Quality Standards can be demonstrated.

When a mobile sampling station is used, a Teflon manifold is needed to conduct air flow from a strategic air sampling point outside the vehicle to the instrumental probe located inside the vehicle. The manifold must intercept air unaffected by the gaseous and particulates produced by the vehicle itself. The manifold projects to the front and about 1 m above the vehicle. Its diameter (~10 cm) must be sufficient to provide instrumental flow requirements without influencing the manifold through-flow. The manifold must be provided with an independent fan-blower system (>1 m^3/min) at its exhaust end to minimize the time lag between air intake and instrumental readout. The instrumental probe distance from the manifold also must be minimized.

2.6.3 Sampling Procedure

Hydrogen sulfide emissions constitute the major air pollutant from areas of geothermal development. In the environment, H_2S is slowly transformed into other chemical species, particularly gaseous SO_2. Measuring the air pollution, therefore, calls for techniques that can simultaneously identify both species in an air mass. Instrumental techniques utilize an internal pump to draw the air sample through the instrument. Species differentiation is usually accomplished by routing incoming air directly into the analysis section and, alternately, through selective traps (typically an SO_2 trap).

Sampling procedures for collecting a variety of atmospheric pollutants are similar. Using the apparatus shown in Figure 2.14, samples are collected by aqueous scrubbing action in the impingers as the air is pumped from the apparatus. Timing is started and air flow is initiated by opening the control valve and adjusting the flow rate indicated on the inlet flowmeter. The flowmeter should be positioned as far upstream as possible to eliminate pressure reduction influences of the pump and scrubbing apparatus. A preliminary particulate filter may be inserted in the flowmeter inlet, depending upon the analysis required. When collecting samples of SO_2, prefiltering is not recommended due to the high reactivity of SO_2 with filter materials.

Several air pollutants may be simultaneously collected from a single air stream to eliminate the internal pollutant variability found when collecting individual samples. For example, a series of scrubbing traps may include both basic and acidic solutions to remove acid and basic-type gases. Mercury samples may be simultaneously collected by inserting the apparatus shown in Figure 2.16 between the flowmeter and the scrubbers. Problems are occasionally encountered when a series of such collectors produce an excessive pressure drop for a single pump. Actual field experience will dictate the sampling train design.

Sampling periods are extended by continuously pumping the air through the collectors. This procedure provides for higher sample concentration where sensitivity is a problem or for measurement of the time integrated air pollutant values.

2.7 SAMPLING FUGITIVE GASEOUS EMISSIONS

In the development of geothermal resources, several field problems have been identified that result in significant gaseous pollutant emissions to the environment. Although attempts are made to minimize or eliminate these emissions, they are somewhat uncontrollable in character. Sources of fugitive emissions include:

- well drilling cave-ins
- steam leaks from well piping
- well venting during short-term power plant shutdowns.

Although emissions from well cave-ins are reduced by land backfilling operations, some emissions continue to evolve from the backfilled zone which may typically be several hundred square meters in area. To sample these sites a large inverted Teflon-lined metal pail (1 m^3) should be used as a gas containment structure. Two access holes are cut in the top of the inverted pail. An insulated Teflon exhaust hose (~13 mm OD) is connected by means of a standard bulkhead fitting assembly, and a pressure relief hose and ball valve (5 cm) are attached. The pail is inverted over the sample site selected and covered with blanket insulation. Appropriate weights are added to secure the system. A dirt seal may be applied to the joint between the pail and ground. The relief valve remains open while the exhaust hose is connected to a condenser system similar to that described in Figure 2.5. The relief valve is closed until the desired flow is established in the condenser. The system is allowed to operate long enough to completely flush the internal pail gases and the condenser before sampling. Sampling for condensate and noncondensable gases is conducted in a manner similar to that previously described (Section 2.4).

Quantitative estimates of total site emissions may be made by measuring the total exhaust flow through the relief valve by using a high-volume, heated flowmeter system and then factoring in the total emissions area. A similar procedure may be implemented for steam leaks from well piping provided a high-temperature plastic containment bag with similar ports can be constructed around the leak.

2.8 SAMPLING PONDS AND STREAMS

Geothermal power plants may discharge small amounts of geothermal liquids or cooling waters to surface holding ponds. Water from such ponds could percolate through the soil and contaminate groundwater supplies. Power plant liquids may also spill into streams. Therefore, ponds and nearby surface waters must be sampled as part of the environmental assessment. Any such discharges must conform to appropriate EPA regulations and permits.

2.8.1 Sample Site Selection

All surface ponds receiving power plant liquids should be sampled. If wells are present near the plant, the groundwater also should be sampled (see Section 5.0). If the possibility of contamination of streams or other surface water by spilled geothermal liquids exists, the streams should be sampled both upstream and downstream from the point of discharge to collect background as well as potentially contaminated water samples. If the stream is so large or stagnant that rapid mixing does not occur, samples should be collected as a function of depth and stream cross section.

2.8.2 Sampling Devices and Procedures

Grab or catch sampling from the edge of the water is the most convenient method for collecting surface samples. A plastic bottle fastened to the end of a wooden or plastic pole is often useful in retrieving a sample away from the shoreline if the water body is quite shallow and if the sediments may be resuspended during sample collection (i.e., muddying the water while wading for a sample).

For deeper water, or for subsurface sampling, a variety of nonmetallic, commercially available water samplers are available. The water sample should not be exposed to metal or rubber components, which can be a source of trace metal contamination. If the particular sampling device may lead to contamination, the sample should be transferred rapidly to recommended containers (see Section 3.0).

The water sample should be filtered immediately after it is collected, preferably in a mobile laboratory or clean-hood type environment where the sample can be cleanly handled. Pressure or vacuum filtration through an all-plastic filtration device through the use of membrane filters (nominal pore size of 0.45μ) is the preferred method. Occasionally, surface water samples of geothermal origin may be saturated with silica, and suspended amorphous silica particulates may clog 0.45μ membrane filters quite rapidly. A coarser prefilter can be used ahead of the 0.45μ filter to remove the larger agglomerates and provide increased filtering capacity.

2.9 SAMPLING SLUDGES AND SOLIDS

A number of solid residues associated with geothermal fluid utilization may accumulate in geothermal power plants or in the immediate surroundings. These residues may contain elevated concentrations of a number of potentially toxic trace elements. For example, scale deposits, cooling tower sludges, pond sediments, or contaminated soils may contain toxic metals and salts in sufficient concentrations to be of environmental concern. Solid byproducts of abatement systems may also contain trace metal contaminants scavenged from geothermal fluids and chemicals used in the abatement processes.

2.9.1 Sample Site Selection

Cooling tower sludges, which deposit in the bottom of cooling towers, can be sampled either from the outside edge or from the ground-level walkway that usually traverses the center of the tower. Since water flow patterns through the bottom of the tower may result in some size sorting of the deposited solids, it is good practice to sample at several locations.

Pond sediments also should be sampled at several locations, preferably on a transect across the pond if it is of substantial size. Stream sediments should be sampled both upstream and downstream from potential sites of contamination from geothermal effluents. For large streams, sampling grids transecting the stream are recommended. It is often desirable to obtain core samples to determine the depth distribution of the constituents of interest.

Scale samples can be taken at any point. Some plants may have removable probes placed in the geothermal flow; when removed a scale sample can be scraped off. If the deposit is banded, or otherwise visually nonuniform, a sample should include the full depth of the scale deposit collected at right angles to the depositing surface. However, as a general rule, it can be assumed that scale deposits within a certain part of the plant are of similar composition because of consistent process conditions. This assumption may not be absolutely reliable for plants that experience repeated operational upsets where the changed process thermodynamics may change the deposition.

2.9.2 Sampling Devices and Procedures

Cooling tower sludges may be grab sampled with a scoop fastened to the end of a pole. Excess water is drained off and the sample transferred to a plastic or glass jar.

Pond or stream sediments can be grab sampled by using a similar procedure if the water is not too deep. If the water is too deep for scoop sampling, a variety of sediment grab samplers are available commercially. Core sampling ported back to the laboratory or extruded and sectioned onsite. The sediments are then placed in plastic or glass jars for storage.

Surface soils or other large solid deposits may be grab sampled with a small shovel or trowel. Subsurface samples may be obtained using commercially available coring devices. An alternative to coring is the trenching technique where a small trench is dug to the desired depth and the one vertical side is left perpendicular to the surface. Subsurface layers may then be sampled in proportion to their abundance from the side of the trench by using a trowel.

2.9.3 Generic Solid Sampling Concerns

When sampling a solid deposit from a geothermal operation, the following principles should be taken into account.

1. If the deposit is large or visually nonuniform, multiple samples and/or core samples are necessary.

2. Prior to sampling, all solid deposits should be visually examined for any indication of nonhomogeneity unless the process that generated the deposit assured reasonable uniformity.

3. In the absence of all other criteria, a solid deposit should be sampled at a location away from the periphery and in a manner to obtain a sample of the bulk material.

4. If, as a result of the analysis on a single grab sample, a serious situation exists, a series of samples that completely describe the deposit should be taken and analyzed.

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3.0 PRESERVATION OF SAMPLE INTEGRITY

Loss of sample integrity can be due to several causes:

- physical leaks (e.g., permitting air to contaminate a gas sample)
- thermodynamic equilibrium (e.g., precipitation of components supersaturated due to temperature changes)
- changes caused by the loss of a particular component (e.g., loss of dissolved CO_2 which may cause the pH to rise)
- chemical reactions (e.g., oxidation of sulfide or ferrous ion)
- contamination (e.g., leaching boron from boron-containing glass containers).

The guidelines for sample preservation are divided into sections according to the state of the sample: gas, liquid, or solid. In general, published information showing data on sample stability in a controlled study is scarce. This is particularly true for geothermal brine samples that are fundamentally different from surface water samples; geothermal brine samples are strongly reducing in redox potential (having no oxygen), while surface water samples are oxidizing in potential (frequently being saturated with oxygen). In some cases the normal EPA-recommended addition of HNO_3 (an oxidizing acid) preservative to geothermal brine samples has caused immediate precipitation as the oxidation state of constituents is abruptly changed. The listed longevity of the samples under the described preservation conditions is based primarily on the evaluation of the experiences of various geothermal chemists. Published data generally are unavailable.

3.1 GAS SAMPLE PRESERVATION

Gas samples may be preserved by either of two generic techniques: reaction in a suitable stabilizing media or preservation as a gas phase in a secured container. Guidelines are given in Table 3.1.

The first option is effective only if the gas is reactive. In geothermal environments the only gases that are commonly stablized this way are H_2S, CO_2, NH_3 or Hg vapor. Figure 3.1 shows a scrubbing bottle that traps gases in reactive solutions. Only one bottle is needed if the throughput is kept moderate.

TABLE 3.1. GAS AND STEAM SAMPLE PRESERVATION GUIDELINES

Gas	Container	Preservation Conditions	Recommended Maximum Holding Time
		--REACTION STABILIZATION--	
$H_2S^{(a)}$	1) P, G	a) Zn acetate, dark, pH >6	7 days
		b) SAOB, sealed container	2 days
	2) G	Deoxygenated NaOH or NH_4OH	7 days
Hg	G	a) Absorbed onto gold-coated beads, Temperature <4°C	28 days
		b) HNO_3, $KMnO_4$, $K_2S_2O_8$ solution trap	28 days
NH_3	P, G	Acidified water trap (HCl, H_2SO_4)	28 days
		--GAS PHASE STORAGE--	
Radon	P, G	Sealed container	28 days
$H_2S^{(a)}$	P(b)	Minimum amount of metal-gas contact in container valve	2 days

---

(a) Assumes sample stream contains no oxygen.

(b) Teflon-lined steel bomb or plastic-aluminum-plastic sandwich constructed sample bag.

The complete trapping of H_2S can be demonstrated by having a second bottle in series that contains a cadmium solution. Any sulfide carryover will result in a brightly colored precipitate in the second bottle.

The second option is the only available preservation (storage) technique for nonreactive gases such as radon. Some reactive gases, in particular H_2S, may be preserved in the gas phase if precautions are observed and the preservation (storage) time is restricted. Any container used to store a gas sample should be filled with the sample to either equal or exceed atmospheric pressure to avoid atmospheric inleakage.

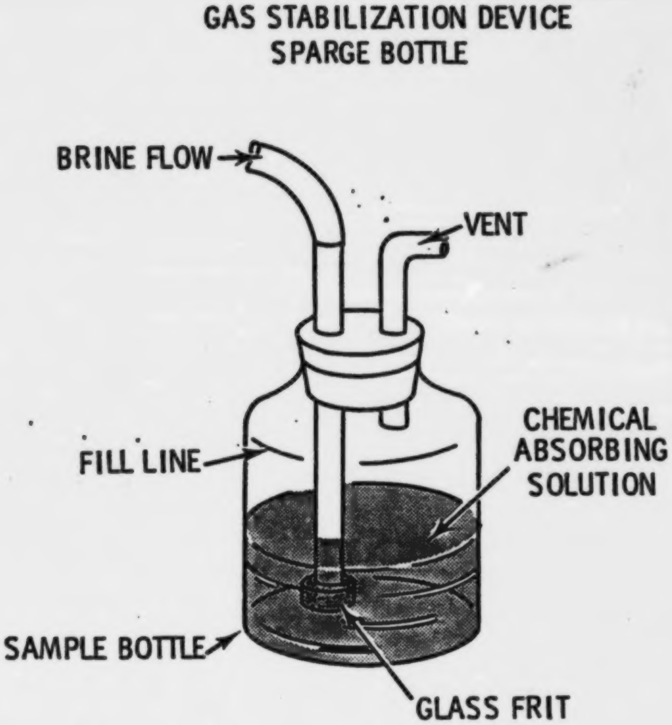
GAS STABILIZATION DEVICE
SPARGE BOTTLE
BRINE FLOW
VENT
CHEMICAL ABSORBING SOLUTION
FILL LINE
SAMPLE BOTTLE
GLASS FRIT

FIGURE 3.1. Scrubber Bottle

3.2 GEOTHERMAL LIQUID SAMPLE PRESERVATION

The guidelines for geothermal liquid sample preservation are summarized in Table 3.2. There are several overall comments:

1. Preservation of steam condensate samples is not usually considered necessary except for those constituents described under the gas and steam sample preservation guidelines. However, if acid is added as a preservative, HCl should be used rather than HNO_3. HNO_3 can oxidize the abundant H_2S to colloidal sulfur and greatly complicate subsequent analysis.

2. When adding a preserving agent, only the very highest purity should be used, and a blank should be analyzed for comparison.

TABLE 3.2. GUIDELINES FOR GEOTHERMAL LIQUID PRESERVATION

Component	Container	0.45 μ Field Filtered	Preservation Conditions	Recommended Maximum Holding Time
TDS	P,G	Yes	None	28 days
pH	P,G	No	None	Immediate
Conductivity	P,G	No	None	28 days
Alkalinity	P,G	No	Fill bottle to top	1 day
Ammonia	P,G	Either	a) H_2SO_4 to pH <2	28 days
			b) HCl 1% by volume	28 days
			c) H_2SO_4, pH <2 Cool 4°C	28 days
Boron	P	Either	None	28 days
Mercury	G	Yes	a) HNO_3 pH <2	28 days
			b) $HNO_3 + 0.05\%\ K_2Cr_2O_7$	28 days
			c) $HNO_3 + KMnO_4 + K_2S_2O_8$(a)	28 days
			d) $HNO_3 + KMnO_4$	28 days
Sulfate	P,G	Yes	None	28 days
Silica	P	Yes	a) Dilute 10-fold	28 days
			b) Acidify 1% HCl	28 days
Metallic Cations	P,G	Yes	a) HNO_3, pH <2	28 days
			b) HCl 1% volume	28 days
Fluoride	P	Either	None	28 days
Chloride	P,G	Either	None	28 days
Sulfide	P,G	Yes	a) Zn acetate, dark, pH >6	7 days
			b) SAOB, sealed container	2 days

(a) This preservative is judged the best for trapping all forms of mercury; see analytical method 4.3.11 for details.

3. Despite the differing philosophies of adding either an oxidizing acid preservative (HNO_3) or a nonoxidizing acid preservative (HCl), it is important to add acid soon after brine sample collection. Acid is effective at arresting the polymerization/precipitation of supersaturated silica that may scavenge trace metals as it comes out of solution. In all cases where HNO_3 is chosen as a preservative, it should be added in a diluted form (1:1 minimum dilution) to minimize oxidation of constituent ions that are normally in the reduced state.

4. Dilution can serve as an alternative and additional effective preservative step, particularly in concentrated brines, because many analyses require sample dilution in the laboratory. Thus, a sample, field-diluted for silica preservation, may serve as a useful sample for other constituents.

5. It is suggested that the main samples to be taken of a geothermal brine would consist of:
   - a filtered, acidified sample (for most metals and possibly SiO_2)
   - a filtered, unacidified sample (most anions, boron, and TDS)
   - a filtered diluted sample (for SiO_2).

   Depending on what else is desired other preserved samples may be required as described.

6. Mercury vapor (from an old laboratory spill or other source) can diffuse through a plastic container and contaminate a water sample (Figure 3.2). For this reason thoroughly cleaned glass containers are recommended for storage of samples intended for mercury analysis.

7. The ability of sulfide and alkalinity to be preserved is subject to disagreement. Low concentrations of sulfide (<1 ppm?) may be difficult to preserve in water and field analysis may be desirable. Fortunately, the lower concentrations are expected to be of less interest than the higher concentrations. Alkalinity stability may vary with water type.

Where more than one option is presented there is insufficient experience available to prefer one over another. The maximum holding time is listed as 28 days simply because the storage data is lacking. Investigators have had satisfactory results using all of the methods in Table 3.2.

For additional information on the preservation of geothermal liquids the Bibliography/References in Section 3.4 may be consulted. EPA publishes guidelines for sample preservation in the Federal Register and updates them when more information becomes available. These guidelines are based on data

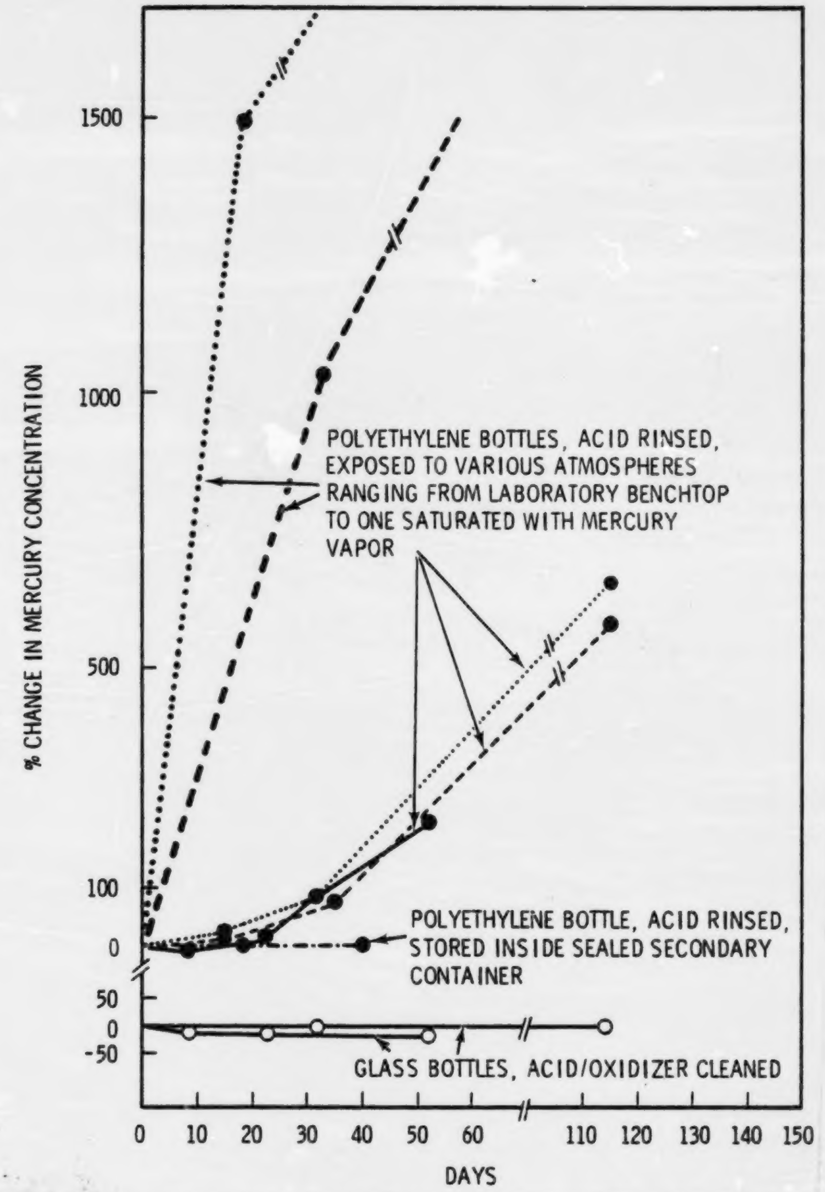

FIGURE 3.2. Comparison of Polyethlyene to Glass as a Storage Container for Saline Solutions of Mercury in the Presence of Contaminated Atmospheres. Initial Concentrations were 2-25 x 10^{-3} ppb. (Data from Bothner and Robertson 1975).

primarily relating to a wide variety of surface waters; however, they should be usable (and are used) for geothermal samples except as they contradict the philosophy of the guidelines described in this section. Compared with normal surface water samples, geothermal samples tend to be:

- much more concentrated and possibly (probably) supersaturated for one or more components
- in a reduced rather than an oxidized state
- of lower bacterial activity (likely sterile).

3.3 SOLID SAMPLE PRESERVATION AND PREPARATION

Methods for preserving and preparing samples are given below.

Preservation

The preservation of solid geothermal samples is judged to be less of a problem than liquids or gases in most cases. In general, three factors that might impair sample integrity are chemical instability, contamination by the container, and reaction with the container materials. Because of these concerns it is recommended that for solid sample preservation:

- a sealable container be used that is constructed of relatively inert materials. The specific material selection may depend on the analysis required of the sample, but would usually consist of glass, stainless steel, Teflon, polyethylene, polypropylene, or other plastics.
- heat and prolonged exposure to the sun be avoided.
- storage time be minimized to the extent practical.

Preparation

Solid samples need to be pretreated before the analytical methods in the next section are applied if the environmental impact of the solid disposal is to be evaluated. This pretreatment (an extraction procedure) is described in Part III, Appendix II of the EPA Hazardous Waste and Consolidated Permit Regulations. It is recommended that the user obtain this procedure directly from the regulations or from EPA in order to be informed of any modifications. Basically a 100-g sample is washed for 24 hours using a pH 5 acetic acid solution; this solution is then analyzed.

3.4 BIBLIOGRAPHY/REFERENCES

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Karkalits, O. C. and B. E. Hankins. 1981. Standardization of Sampling and Analysis of Geopressured Fluids. Part II: Monitoring of Geopressured Wells. GRI-80/0061, Gas Research Institute.

Kindle, C. H. and E. M. Woodruff. 1981. Techniques for Geothermal Liquid Sampling and Analysis. PNL-3801, Pacific Northwest Laboratory, Richland, Washington.

Presser, T. S. and I. Barnes. 1974. Special Techniques for Determining Chemical Properties of Geothermal Water. WRI-22-74, U.S. Geological Survey, Menlo Park, California.

4.0 ANALYTICAL METHODS

This section contains procedure write-ups and rationale for selecting the analytical methods specified.

The first subsection (4.1) details procedures for water quality parameters not identifiable with unique chemical species. The parameters addressed are: alkalinity, specific conductance, total dissolved solids, pH, and "scale inhibitors."

The second subsection (4.2) addresses the nonmetal analytes of concern to geothermal liquid samples, namely, ammonia, chloride, fluoride, sulfate, sulfide, and nitrate (even though appreciable nitrate is not found in geothermal brines).

The third subsection (4.3) deals with metals and metalloid element analyses. In most cases, atomic absorption spectroscopy and plasma emission spectroscopy are the methods deemed most suitable.

The fourth subsection (4.4) contains recommended techniques and procedures for monitoring or analyzing gaseous samples.

4.1 WATER QUALITY PARAMETERS

4.1.1 Alkalinity

Method Title

Neutralization Titration

Method Summary

An appropriate volume of sample is titrated with standard acid to a pH = 4.5 end point as soon as possible after collection.

Analytical Range

20 mg $CaCO_3$/l

Sample Range

Depends on value of alkalinity; sample volume chosen such that ~0.7 milliequivalent of titrant will be used. (Assumes use of 10-ml buret)

Precision

±5-10%

Published References

EPA #310.1 or 310.2, 1978 NPDES approved, Storet #00410
APHA 14th Edition, p. 278-282 (1975)
ASTM D1067A, p. 111-113 (1977)

Potential Interferences and Comments

Total alkalinity, defined as acid neutralizing capacity, is measured by acidimetric titration to a predetermined end point, usually pH = 4.5 or the methyl orange indicator color change. Alkalinity is mainly due to HCO_3^- and $CO_3^{=}$, and titration results are interpreted accordingly. The presence of other basic species and/or hydrolyzable metal ions such as Fe^{3+} (derived from Fe^{2+} via air oxidation) may compromise the usual interpretation of results. Geothermal samples that have a pH <8 may have contributions to alkalinity from HS^-, HPO_4^{2-}, and hydrolyzable cations besides HCO_3^-. Samples that have pH >8 may have contributions to alkalinity from $CO_3^{=}$, BO_2^-, and $HSiO_3^-$ in addition to the species mentioned above.

Samples that have a pH >8.3 are usually titrated first to a pH = 8.3 end point (phenolphthalein) and finally to the pH = 4.5 end point. The neutralizing capacity of the first titration is interpreted as due to CO_3^{2-}. Total alkalinity (pH = 4.5 end point) is interpreted as the sum of HCO_3^- and CO_3^{2-}. In mathematical terms, the bicarbonate alkalinity is calculated as:

mmols HCO_3^- = total mequiv acid used - 2 x mmols $CO_3^=$, and
mmols $CO_3^=$ = mequiv acid used to reach phenolpthalein end point.

Alternative Analytical Method

1. Use of the methyl orange end point instead of potentiometric end point (pH 4.5) is acceptable.

2. An automatic titrator with provision for recording the entire titration curve can be useful in determining the extent of alkalinity contributions due to noncarbonate species.

3. Back titration schemes have been worked out that more reliably address the question of noncarbonate alkalinity contributions. For example, after titration to pH 4.5, the solution is acidified to pH 3.7 and boiled (or nitrogen purged) to expel CO_2. Standard base (NaOH) is then used to bring the pH back to its original value. The amount of base used in this back titration is a measure of noncarbonate and nonsulfide contributions to alkalinity.

Reagents

0.1 N HCl or H_2SO_4
Na_2CO_3
(methyl orange indicator)
(phenolphthalein indicator)
pH standards

Equipment

pH meter and electrodes
(recording titrator)
10.0-ml buret

Procedure

Preparation and Standardization of Reagent Solutions

Sodium carbonate solution, approximately 0.05 N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 h and cooled in desiccator) into a 1-l volumetric flask and dilute to mark.

Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HCl to 1 l with distilled water. Standardize versus 15.0 ml N Na_2CO_3 solution mixed with about 25 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3 to 5 min under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where A = g Na_2CO_3 weighed into 1 l
B = ml Na_2CO_3 solution
C = ml acid used to inflection point.

Titration of Sample

Sample Size

Use a sufficiently large volume of titrant (>5 ml in a 10-ml buret) to obtain good precision while keeping volume low enough to permit sharp end point.

For <600 mg CO_3^{2-}/l use 0.02 N titrant.
For >600 mg CO_3^{2-}/l use 0.1 N titrant.
A preliminary titration is helpful.

Potentiometric Titration

Place sample in flask by pipetting with pipet top near bottom of flask.

Measure pH of sample.

Add standard acid, being careful to stir thoroughly but gently to allow needle to obtain equilibrium.

Titrate to pH 8.3. Record volume of titrant.

Continue titration to pH 4.5. Record total volume of titrant used.

Calculation

$$\text{mg } CO_3^{=}/l = \frac{V_1 \times N \times 60{,}000}{V_s}$$

and

$$\text{mg } HCO_3^{-}/l = \frac{(V_2 - 2V_1) \times N \times 61{,}000}{V_s}$$

where V_1 = ml standard acid required to reach pH = 8.3
V_2 = total volume (ml) of standard acid required to reach pH = 4.5
V_s = sample volume (ml)
N = normality of standard acid used.

Some analysts prefer to express results as "total alkalinity" in terms of $CaCO_3$. The calculation then becomes:

Total alkalinity (as mg $CaCO_3$/l) =

$$\frac{[V_2 \text{acid (ml)}] \times (\text{N acid}) \times 50{,}000}{\text{Sample volume (ml)}}$$

4.1.2 Specific Conductance

Method Title

Conductivity Meter with Calibrated Cell

Method Summary

Specific conductance of a sample is measured using a self-contained conductivity meter, Wheatstone bridge-type or equivalent.

Analytical Range

>0.5 μS/cm

Sample Size

25 ml (depends on cell configuration)

Precision

<±10%

Published Reference

EPA #120.1, 1971 NPDES approved,
  Storet #00095
ASTM D-1125-77 (1977)
APHA 205 (1976)

Potential Interferences and Comments

Solution conductance is highly temperature dependent. For this reason, conductivity measurements should be performed at a known temperature (preferably 25°C). The temperature at which the conductance is measured should be reported along with the conductance value measured.

Conductivity cell should be kept clean and thoroughly rinsed (wet) between measurements.

Specific conductance can also be changed by the dissolved state of certain gases such as NH_3 and CO_2. The measurement precision in highly concentrated geothermal brines may be worse than that quoted.

Alternative Analytical Methods

None

Reagents

KCl (for calibrating cell)
Deionized water

Equipment

Conductivity meter and cell

Procedure

Determination of cell constant: Rinse the conductivity cell with at least three portions of 0.01 M KCl solution. Adjust the temperature of a fourth portion to 25.0 ±0.1°C. Measure the resistance of this portion and note the temperature. Compute the cell constant, C:

$$C = \frac{0.001413R_{KCl}}{1 + 0.0200(T-25)}$$

Conductivity measurement: Rinse the cell with one or more portions of the sample to be tested. Adjust the temperature of a final portion of the sample to 25.0 ±0.1°C. Measure the resistance of the sample and note the temperature.

Calculation

The following directions apply to the commonly used Wheatstone bridge instruments. Instruments may be calibrated to read conductivity (or conductance) directly; in that case follow the manufacturer's instructions.

The conductivity G, in µS/cm, is given by the equation:

$$G = \frac{1{,}000{,}000\ C}{R\ [1 + 0.0200(T-25)]}$$

where R = resistance of the sample, ohms
C = cell constant
T = temperature, °C.

4.1.3 Total Dissolved Solids (TDS)

Method Title

Gravimetric

Method Summary

The sample is filtered through a membrane filter. A known volume of the filtrate is evaporated in a tared drying dish, oven dried (180°C), and weighed after cooling in a desiccator.

Analytical Range

>4 mg/l

Sample Size

Variable; if possible sample size should be chosen so that ~100 mg of residue are obtained.

Precision

±5%

Published References

EPA #160.3, 1971 NPDES approved, Storet #00500
ASTM D1888-67A (1977)
APHA 208 B, C (1976)

Potential Interferences and Comments

Highly mineralized waters with considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to ensure complete conversion of bicarbonate to carbonate.

Too much residue in evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

Under certain conditions silica will settle out of a filtered brine solution upon standing. For this reason, among others, TDS determinations should be made as soon as possible after sample collection or performed on a diluted (at time of acquisition) sample if the source is high-temperature (high silica) geothermal brine.

Alternative Analytical Methods

If a complete chemical analysis for major cations and anions is available, TDS can be calculated. This calculation should include as a minimum: Na, K, Li, Sr, Mg, Ca, Fe, Cl, SiO_2, CO_3, HCO_3, SO_4 for geothermal waters. The agreement between calculated and experimental values may not be exact since some components may volatilize or convert to other forms during the drying at 180°C.

Reagents

Desiccant (anhydrous calcium sulfate, silica gel, P_2O_5, etc.)

Equipment

Analytical balance
Drying oven
Desiccator
Evaporating dishes
Filter apparatus

Procedure

Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

Preparation of evaporating dishes: If volatile residue is also to be measured, heat the clean dish to 550 ±50°C for 1 h in a muffle furnace. If only filterable residue is to be measured (the common value), heat the clean dish to 180 ±2°C for 1 h. Cool in desiccator and store until needed. Weigh immediately before use.

Filter the sample through the glass fiber filter and rinse the filter with three 10-ml portions of distilled water. Transfer a suitable measured volume of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath (100°C).

Dry the evaporated sample for at least 1 h at 180 ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg or the desired accuracy level.

Calculation

Calculate filterable residue as follows:

$$\text{mg/l} = \frac{(A - B) \times 1000}{C}$$

where A = weight of dried residue + dish, mg
B = weight of dish, mg
C = volume of sample used, ml.

4.1.4 pH Measurements

Method Title

Potentiometry

Method Summary

The pH of a solution is determined by measuring the e.m.f. developed between glass and reference electrodes.

Analytical Range	Sample Size
1-12 pH units	10 ml

Precision	Published Reference
±0.10 pH unit	EPA #150.1, 1978 NPDES approved, Storet #00400 (on site) #00403 (lab.) APHA 424 (1976) ASTM D-1293-65 (1977)

Potential Interferences and Comments

Temperature affects pH measurements. The meter-electrode system should be standardized with known buffers at the same temperature as the sample tested. The temperature at which pH measurements are made should be recorded along with pH value. Typical glass electrodes undergo a sodium interference in high pH (>12) samples. pH measurements should be made as soon as possible after sample acquisition particularly if it is a geothermal brine that may lose CO_2 on standing. Some of these samples have been known to shift 2 pH units between field and laboratory measurements. Modern, portable instruments are readily available for field measurements (which are recommended).

Poorly buffered samples may not be amenable to the stated precision of ±0.10 pH unit. Agreement between field and laboratory values for geothermal brines will usually not be within 0.1 pH unit.

Alternative Analytical Method

pH paper may be used if uncertainty of 0.3 to 0.5 pH unit is tolerable.

Reagents	Equipment
Standard pH buffers	pH meter
Deionized water	Glass electrode
	Reference electrode

Procedure

Standardize the meter and electrode system with standard buffers that bracket the expected pH of sample. Consult instrument manufacturer's directions for calibration and standardization procedure. Be sure to thoroughly rinse electrodes with deionized water between measurements. Note and record pH value and temperature of sample.

Calculation

None required.

4.1.5 Scale Inhibitors

Due to the proprietary nature of commercial products used for cooling water treatment, no comprehensive and general analysis procedure can be recommended here.

Normally, the manufacturer supplies sufficient details so that the customer can monitor or analyze for the active ingredient(s) in commercial formulations. Generally, a relatively simple colorimetric or titrametric analysis is specified.

4.2 NONMETAL ANALYSIS

4.2.1 Ammonia (NH_3 - NH_4^+)

Method Title

Ammonia Selective Electrode

Method Summary

The sample containing NH_3 or NH_4^+ is rendered basic with NaOH. The electric potential of ammonia gas sensing electrode versus a reference electrode (built into the ammonia sensing electrode itself) is measured with an electrometer pH meter or a millivolt meter. NH_3 (NH_4^+) content of sample is determined from calibration curve obtained from appropriate standards.

Analytical Range	Sample Size
0.1-10,000 mg NH_3/l	$\geq$5 ml

Precision	Published Reference
~3%	EPA #350.3 EPA Storet #00610

Potential Interferences and Comments

Volatile amines and Hg^{2+} interfere. Color and turbidity have no effect on measurement - a decided advantage over colorimetric analysis, where the sample must be subjected to filtration or distillation prior to actual analysis of colored or turbid samples. The lifetime of the electrode is variable and a spare may be desirable.

Alternative Analytical Methods

1. Nesslerization following distillation would be a suitable method for determining NH_3-N in brines. Nesslerization without distillation would be applicable to steam condensate and other samples low in total solutes (APHA 418B, 1975). Some brines have NH_3 concentrations high enough to permit this direct Nesslerization procedure (with the use of Rochelle's salt) to give satisfactory results. If a geothermal plant laboratory prefers this procedure, satisfactory performance could be demonstrated through standard addition tests.

2. Colorimetric phenate (APHA 418C) following distillation is another favorable method for analyzing brines. Again, low solute-containing

samples such as steam condensate might not require the distillation step.

Reagents

NH_3-free DI water
10 N NaOH
Stock NH_4Cl solution

Equipment

Electrometer (pH meter) with expanded mV scale
NH_3 selective ion electrode such as EIL Model 8002-2 or Orion Model 95-10
Magnetic stirrer and stir bar

Procedure

Preparation of Standards

Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

Calibration standards prepared by serial dilution of stock NH_4Cl should be matrix matched if very saline samples are to be analyzed. Synthetic ocean water or appropriate concentration of NaCl is recommended.

Standard additions should be used occasionally to check accuracy of analysis.

Calibration of Electrometer

Place 100 ml of each standard solution in clean 150-ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10 N sodium hydroxide solution while mixing.

The pH of the solution after the addition of NaOH must be above 11. Keep electrode in the solution until a stable reading is obtained.

Caution: Sodium hydroxide must not be added prior to electrode immersion because ammonia may be lost from a basic solution.

Repeat this calibration procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH_3-N/l on the log axis versus the electrode potential developed in the standard on the linear axis. Start with the lowest concentration at the bottom of the scale.

Calibration of a Specific Ion Meter

Follow the directions of the manufacturer for the operation of the instrument.

Sample Measurement

Follow the same procedure as in the calibration step for 100 ml of sample in 150-ml beakers. Record the stabilized potential of each unknown sample and use the standard curve to convert the potential reading to the ammonia concentration. If a specific ion meter is used, read the ammonia level directly in mg NH_3-N/l.

Smaller volumes of standard solutions and samples can be used with appropriate scaling of 10 N NaOH added.

Calculation

As indicated above, read NH_3-N concentration directly from semilogarithmic calibration curve or from properly calibrated specific ion meter.

4.2.2 Chloride

Method Title

Titration, Silver Nitrate

Method Summary

Standard silver nitrate solution is used to titrate a suitable aliquot of chloride-containing sample.

Analytical Range

1-20 mg Cl

Sample Size

Depends on concentration

Precision

±4%

Published References

ASTM D512B (1977)
APHA 408A and C (1975)

Potential Interferences and Comments

Other anions which interact strongly with Ag^+, either through precipitation (e.g., Br^-, I^-, HPO_4^{2-}, $S^=$) or complex formation (e.g., CN^-, $S_2O_3^=$), will bias results (high). For geothermal brines, no problem is anticipated. Other fluids, such as steam condensate, may not be analyzable due to high $S^=/Cl^-$ ratio. Consult APHA reference for further discussion.

Alternative Analytical Methods

1. The use of $Hg(NO_3)_2$ instead of $AgNO_3$ as titrant is equally satisfactory. Same interferences, range, and precision are expected. Potential hazards of dealing with mercury salts are partially mitigated by expense of reagent-grade $AgNO_3$. For discussion of chloride analysis with $Hg(NO_3)_2$ titrant, see EPA #325.3, 1978 NPDES approved, Storet #00940.

2. Direct measurement of Cl^- by selective ion electrode potentiometry is not recommended for geothermal because of interference (i.e., sulfide). An electrode may be used as end point monitor in either $AgNO_3$ or $Hg(NO_3)_2$ titration.

3. For low levels of Cl^-, as in steam condensate, ion chromatography would be appropriate. Ion chromatography is a powerful and increasingly popular tool for anion analysis. Analysis of brine samples is also possible, but samples need to be diluted so that chloride content of the aliquot actually injected is in the range of 1 to 10 ppm.

4. Samples containing chloride in the 1 to 200 ppm range can be analyzed by EPA procedure 325.2. There is no obvious advantage to this procedure, except when automated in such a device as the "Technicon Auto Analyzer" system; 20 to 30 samples per hour can be analyzed.

Reagents

Standard $AgNO_3$ solution
Standard NaCl - for standardizing $AgNO_3$ solution
K_2CrO_4 (50 g/l) - indicator
Phenolphthalein indicator (10 g/l in alcohol)
NaOH solution - for pH adjustment
H_2SO_4 solution - for pH adjustment

Equipment

25 ml buret
Magnetic stirrer - stir bars
Clean labware
Pipets

Procedure

Pipet a volume of sample containing between 1 and 20 mg Cl into a 250-ml Erlenmeyer flask. Add stir bar and dilute to ~50 ml with DI water. Add 2 drops phenolphthalein indicator; adjust pH with NaOH and/or H_2SO_4 to ~pH 8 (this pH corresponds to just a trace of pink, phenolphthalein color). Add 1.0 ml K_2CrO_4 solution. Titrate with standard 0.014 N $AgNO_3$ until the red-brown color of Ag_2CrO_4 persists while stirred magnetically. Record volume $AgNO_3$ used.

The $AgNO_3$ solution should be standardized against primary standard NaCl. The procedure is the same as used for samples. 25.0 ml of a standard NaCl solution containing ~0.40 mg Cl^- ml is an appropriate aliquot for standardization.

Calculation

$$\frac{V \times N \times 35500}{S} = \text{mg Cl}^-/\text{l}$$

where V = volume $AgNO_3$ used (ml)
N = normality of $AgNO_3$ (~0.014 N)
S = volume of original sample taken (ml).

4.2.3 Fluoride

Method Title

Distillation followed by SPADNS[a] Colorimetric (or selective ion electrode)

Method Summary

Sample is rendered acidic (H_2SO_4) and distilled. Distillate containing HF (and/or H_2SiF_6) is treated with mixed acid-zirconyl-SPADNS reagent, and absorbance measured at 570 nm. Fluoride content is proportional to amount of bleaching of Zr-SPADNS complex observed.

Analytical Range

0.1-1.4 mg F/l

Sample Size

300 ml

Precision

~10%

Published References

EPA #340.1, 1978 NPDES and SDWA approved,
  Storet #00951 (total)
  #00950 (dissolved)
APHA 14th Ed., p. 387-394 (1975)
ASTM D1179, p. 339-342 (1977)

Potential Interferences and Comments

The distillation step largely eliminates interferences. However, distillation temperature should be kept below 180°C to avoid excessive sulfate carryover. Addition of Ag_2SO_4 to distillation pot is recommended to render chloride nonvolatile when dealing with brine samples.

Analysis of concentrated brines without the distillation step has resulted in poor precision with factors of two-to-ten differences (Kindle and Woodruff 1981; Karkalits and Hankins 1981). Direct analysis by the popular selective ion electrode, without the awkward distillation step, may very well be suitable for low salinity brines (5000 ppm TDS?) and could be demonstrated suitable, or unsuitable, by a comparative distillation versus direct analysis. In the absence of such a comparative test direct fluoride results should be interpreted with consideration given to potential two- to tenfold discrepancies between laboratories.

(a) SPADNS = sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate.

Alternative Analytical Methods

1. Following distillation, the fluoride content of the distillate may be reliably determined with fluoride selective ion electrode methodology. Each of the above references outlines suitable procedures.

2. Ion chromatography can be used reliably for fluoride if the solution analyzed is free of complexing metal ions such as Al^{3+} or Fe^{3+} and fluoride concentration is >0.5 mg F/l. Direct analysis of brines without the distillation step may be possible if chromatographic conditions are suitable; i.e., situations where Cl^-/F^- ratio is too large must be avoided and the capacity of separator columns must not be exceeded.

Reagents	Equipment
Fluoride standard (NaF)	Distillation apparatus
SPADNS reagent	Spectrophotometer or colorimeter capable of operation in 570 nm region.
$ZrOCl_2 \cdot 8H_2O$	
HCl	
Ag_2SO_4	
H_2SO_4	
$NaAsO_2$	

Procedure

Preparation of Reagent Solutions

SPADNS solution: Dissolve 0.958 g SPADNS in distilled water in a 500-ml volumetric flask and dilute to the mark. The solution is stable indefinitely if protected from direct sunlight.

Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in ~25 ml distilled water in a 500-ml volumetric flask. Add 350 ml conc HCl and dilute to the mark with distilled water.

Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 yr.

Reference solution: Add 10 ml SPADNS solution to 100 ml distilled water. Dilute 7 ml conc HCl to 10 ml and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.

Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water in a 1-l volumetric flask and dilute to the mark with distilled water (CAUTION: TOXIC - avoid ingestion).

Preparation of Stock and Standard Fluoride Solutions

Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride, NaF, in distilled water in a 1-l volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.1 mg F^-.

Standard fluoride solution: Place 100 ml stock fluoride solution in a 1-l volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.010 mg F^-.

Preliminary Distillation

Place 400 ml distilled water in the distilling flask.

Carefully add 200 ml conc H_2SO_4 and swirl until contents are homogeneous.

Add 25 to 35 glass beads (boiling initiators), connect the apparatus (Figure 4.1) making sure all joints are tight.

Heat slowly at first then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

Cool to 120°C or below.

Add 300 ml sample, mix thoroughly, distill as above until temperature reaches 180°C. Do not heat above 180°C to prevent sulfate carryover.

Add Ag_2SO_4 at a ratio of 5 mg/mg Cl when high chloride samples are distilled.

Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.

High fluoride samples may require that the still be flushed by using distilled water and combining distillates.

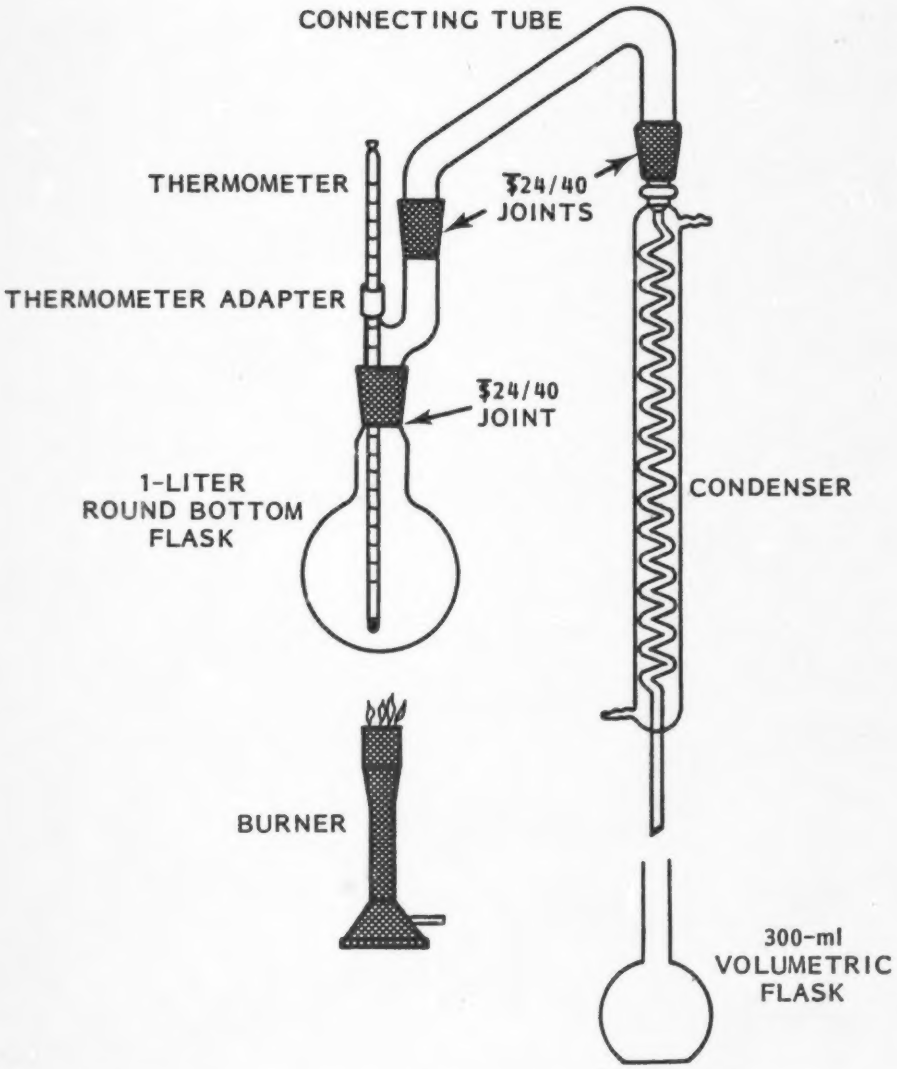
CONNECTING TUBE
THERMOMETER
$24/40 JOINTS
THERMOMETER ADAPTER
$24/40 JOINT
1-LITER ROUND BOTTOM FLASK
CONDENSER
BURNER
300-ml VOLUMETRIC FLASK

FIGURE 4.1. Direct Distillation Apparatus for Fluoride

Colorimetric Determination

Prepare fluoride standards in the range 0 to 1.40 mg/l by diluting appropriate quantities of standard fluoride solution to 50 ml with distilled water.

Pipet exactly 5.00 ml each of SPADNS solution and zirconyl-acid reagent or 10.00 ml of the mixed acid-zirconyl-SPADNS reagent to each standard and mix well.

Set photometer to zero with reference solution and immediately obtain absorbance readings of standards.

Plot absorbance *versus* concentration. Prepare a new standard curve whenever fresh reagent is made.

If residual chlorine is present, pretreat the sample with 1 drop (0.05 ml) $NaAsO_2$ solution per 0.1 mg residual chlorine and mix. Sodium arsenite concentrations of 1300 mg/l produce an error of 0.1 mg/l at 1.0 mg/l F^-.

Use a 50-ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve. Add 5 ml SPADNS solution and 5 ml zirconyl-acid reagent *or* 10 ml mixed acid-zirconyl-SPADNS reagent to sample. Mix well. Measure absorbance of sample versus reference solutions.

Calculation

Use the standard curve to read the concentration in the 50-ml sample. Calculate as follows:

$$\text{mg } F^-/\text{l} = \frac{\text{mg}F^- \times 1000}{\text{m sample}}$$

When a sample (ml sample) is diluted to a volume (B) and then a portion (C) is analyzed, use:

$$\text{mg}F^-/\text{l} = \frac{\text{mg}F^- \times 1000}{\text{mL sample}} \times \frac{B}{C}$$

4.2.4 Nitrate

Method Title

Ion Chromatography

Method Summary

Aqueous sample containing nitrate is injected into ion chromatograph fitted with anion-exchange separator column. Nitrate ion is identified by its characteristic retention time and quantified by comparison of peak heights (or areas) with those of known standards.

Analytical Range	Sample Size
>0.02 mg/l	5 ml

Precision	Published Reference
±10%	Dionex® Application Note #8

Potential Interferences and Comments

Since nitrate (of problem concentrations) has not been found in geothermal brines, the ion chromatography method specified here is also applicable to other waters. The high chloride/nitrate ratio of geothermal brines would make detection of nitrate very difficult even if it were present near the detection limit quoted. No direct experience in nitrate analyses in geothermal brines was available during the evaluation phase of this project.

Alternative Analytical Methods

Many colorimetric methods for nitrate have been developed and successfully employed. All are relatively difficult due to the complexity of procedures, interferences, and limited working ranges.

The most popular, nonautomated colorimetric methods are based on: 1) Brucine (EPA Method 352.1) and 2) cadmium reduction (EPA Method 353.3). The Brucine method has a working range of 0.1 to 2 mg NO_3^--N/l. Cadmium reduction method working range is 0.01 to 1.0 mg NO_3^--N/l.

A selective ion electrode for nitrate is commercially available for use with the samples with a NO_3 content between 1 and 50 mg NO_3-N/l (ORION Model 93-07).

® Dionex Corporation, Sunnyvale, California

Reagents

$NaNO_3$ (for preparing standards)
Deionized H_2O

Equipment

Ion chromatograph with anion separator column
Syringes

Procedure

Turn on ion chromatograph pump and equilibrate system with effluent to be used. Inject sample and standards sequentially.

Calculation

Calculate NO_3^- content of sample by comparison of peak heights (or areas) with those of standards.

4.2.5 Sulfate

Method Title

Turbidimetric - Direct

Method Summary

A suitable aliquot of acid-preserved sample is treated with $BaCl_2$. The turbidity due to the $BaSO_4$ suspension formed is determined by a spectrophotometer (390 nm) and compared with the turbidity found from similarly treated matrix-matched standards.

Analytical Range

10-100 mg $SO_4^=$/l

Sample Size

$\leq$50 ml

Precision

5% with care

10% more typical

Published References

EPA #375.4, 1971 NPDES approved,
Storet #00945
ASTM D516-B, p. 494-496 (1977)
APHA 427C, p. 496-498 (1975)

Potential Interferences and Comments

Any suspended matter or color in the sample will interfere. Silica in concentrations over 500 mg/l will interfere. Other barium precipitable anions such as carbonate and phosphate are not expected to be a problem in acidified geothermal brines. The turbidimetric method recommended here (and elsewhere) is chosen as a compromise between accuracy and convenience. Sulfate measurements in concentrated brines have shown decreased precision, but the reasons are not clear. If sulfate levels are a potential problem in a concentrated brine it might be wise to test any method using spike recoveries.

Alternative Analytical Method

1. Gravimetric determination of $SO_4^=$ as $BaSO_4$. This is probably the oldest and most accurate method for the analysis of sulfate. The time needed and multitude of sample work-up steps make this method inconvenient and not worth the effort unless the highest precision and accuracy are required (EPA PB297686, p. 379-81, 1979).

2. Turbidimetric titration. This is a straightforward variant of the direct turbidimetric method. Turbidity is used to monitor the course of sample titration. $BaCl_2$ titrant is used. End point is taken when incremental

additions of titrant cause no further increase in turbidity. This method is capable of better accuracy and precision than the direct one-point turbidimetric method, but is much more cumbersome.

3. Ion chromatography. This is a convenient and reliable method for samples in which the chloride content is not overwhelming (Dionex Application Note #3, 1978).

Reagents

$BaCl_2 \cdot 2H_2O$
Glycerin or sodium carboxymethylcellulose
NaCl
Na_2SO_4 (for preparing standards)
Ethanol or isopropanol
Na_2CO_3

Equipment

Spectrophotometer, nephelometer, or filter colorimeter capable of measurement at 390 to 420 nm
Cuvets for above
Magnetic stirrer
Stopwatch

Procedure

Preparation of Reagent Solutions

Conditioning reagent: Place 30 ml conc HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol, and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.

Sodium carbonate solution (~0.05 N): Dry 3 to 5 g primary standard Na_2CO_3 (180°C) for 4 h and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1-l volumetric flask, dissolve and fill to the mark with distilled water.

Preparation of Standards

Standard sulfate solution (1.00 ml - 100 μg SO_4): Prepare by either technique A or B (B is easier for most laboratories).

A. Standard SO_4 Solution From H_2SO_4

A.1. Standardize Sulfate Solution from H_2SO_4 (standard sulfuric acid, 0.1 N): Dilute 3.0 ml conc H_2SO_4 to 1 l with distilled water. Standardize versus 40.00 ml 9 of 0.05 N Na_2CO_3 solution plus about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where A = g Na_2CO_3 weighed in 1 l
B = ml Na_2CO_3 solution
C = ml acid used to inflection point.

A.2. Make Standard Acid (0.02 N): Dilute appropriate amount of standard acid, 0.1 N to 1 l (200.00 ml if 0.1000 N). Check by standardization against 15 ml of 0.05 N Na_2CO_3 solution.

A.3. Final Dilution: Place 10.41 ml of the standard sulfuric acid (0.02 N) in a 100-ml volumetric flask and dilute to the mark. This is now the standard sulfate solution where 1.00 ml = 100 µg SO_4.

B. Standard Sulfate Solution From Na_2SO_4

Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1-l volumetric flask and dilute to the mark with distilled water.

Formation and Measurement of Barium Sulfate Turbidity:

1. Place 100-ml sample, or a suitable portion diluted to 100 ml, into a 250-ml Erlenmeyer flask.
2. Add exactly 5.0 ml conditioning reagent.
3. Mix in the stirring apparatus.
4. While the solution is being stirred, add a measured spoonful of $BaCl_2$ crystals (approximately 0.25 ml) and begin timing immediately.
5. Stir exactly 1.0 min at constant speed to allow for solids (turbidity) formation.
6. Immediately after the stirring period has ended, pour solution into absorbance cell.
7. Measure turbidity at 30-s intervals for 4 min.

Preparation of Calibration Curve

Use standard sulfate solution to prepare calibration curve. Space standards at 5 mg/l increments in the 0 to 40 mg/l sulfate range. Above 50 mg/l the accuracy decreases and the suspensions lose stability.

Check reliability of calibration curve by running a standard with every 3 or 4 samples.

Correction for Sample Color and Turbidity

Run a sample blank using the procedure above without the addition of barium chloride.

Calculation

Read mg SO_4^{2-} from calibration curve

$$\frac{\text{mg } SO_4^{2-}}{\text{l}} = \frac{\text{mg } SO_4^{2-} \times 1000}{\text{ml sample}}$$

4.2.6 Sulfide ($H_2S-S^=$)

Method Title

Iodometric Titration

Method Summary

A zinc acetate preserved sample is used. The ZnS, $Zn(OH)_2$ suspension is added to an acidic iodine (I_3^-) solution where the Zn precipitates dissolve and the liberated H_2S is rapidly oxidized to elemental sulfur. The excess I_3^- is then back-titrated with standard thiosulfate.

Analytical Range	Sample Size
>3 mg S	Sufficient volume of $ZnS/Zn(OH)_2$ suspension to contain >3 mg S

Precision	Published Reference
±5%	EPA #376.1, 1978 NPDES approved, Storet #00745 (total) #00746 (dissolved)

Potential Interferences and Comments

Reducing agents other than $S^=$, if present, will bias results high. Such species as sulfite, thiosulfate, hydrosulfite as well as oxidizable metal ions, e.g., Fe(II), Cu(I), are the reducing agents most often cited. Precautions against excessive oxygen and light exposure should be observed. If other reducing agents are present, this analysis would tend to overestimate the true $S^=$ content. To get a better estimate of sulfide alone, the $ZnS/Zn(OH)_2$ suspension should be filtered or centrifuged and the filter-cake resuspended in DI water followed by treatment with excess I_3^- and acid and back titration with thiosulfate as described in this procedure. It is recommended that this interference check be performed on each sample stream to identify the presence/absence of other reducing agents (interferences).

The preserved sample suspension must be rendered acidic immediately before I_3^- is added. A variety of products occur, not just the anticipated elemental sulfur, when I_3^- is added to a basic solution of sulfide causing erroneous results. Frequent (e.g., weekly) restandardization of the iodine and thiosulfate solutions used is needed to ensure accuracy.

Alternative Analytical Methods

1. Precipitation titrimetry using either $AgNO_3$ or a Pb(II) salt titrant with potentiometric end-point detection work wells if the chloride content is low (steam samples) and the analysis is performed before sample oxidation occurs. Preservation solutions must be chosen carefully; e.g., SAOB(a) preserved samples cannot be used with Ag^+ titration due to rapid reduction of Ag^+ by ascorbate.

2. Sulfide selective ion electrode methodology, capable of analysis over a wide dynamic range and simple and convenient in principle, generally has not been accepted by geothermal fluids analysts. A possible reason is that reliable use of sulfide SIE methodology is more complicated than the literature suggests.

3. For higher sulfide levels (e.g., >100 ppm), gas chromatography with thermal conductivity detection has been successfully employed for analyzing steam condensates and noncondensable gases (H_2S) in steam flows.

4. For low sulfide levels, the methylene blue color comparison method has the advantage from the standpoint of convenience and reliability. (EPA-600, 4-79-020, PB297686, Method 376.2, p. 387-388, 1979.)

5. Flame photometric detectors for sulfur species in the gas phase are capable of very low detection limits and high selectivity. Such detectors are relatively expensive. For any of these low-level instrumental sulfide analysis techniques, the problem of preparation and preservation of appropriate standards is significant although advances are being made in this area of gaseous H_2S standards.

6. A few investigators (notably from the U.S. Geological Survey in Menlo Park, California) recommend a method for steam samples involving oxidation of sulfide to sulfate (via H_2O_2) followed by gravimetric analysis of SO_4^{2-} as $BaSO_4$. The advantage of this approach (no standard is needed) is seemingly outweighed by the many unit operations and time involved. However, the field sampling operation may be simple to the practiced operator.

7. Gaseous H_2S has also been determined without recourse to any trapping solutions. Most prominent are systems based on the darkening of

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(a) SAOB = sulfide antioxidant buffer (basic, ascorbate, and complexant containing solution).

moist lead acetate paper (Houston Atlas Co., Houston, Texas) and amperometric determination of gaseous H_2S which passes through a suitable gas permeable membrane into an electrolyte (Interscan Corp., Chatsworth, California) The difficulty of quantifying lead acetate paper darkening systems and the need for gaseous calibration standards for the amperometric method are the chief shortcomings of these direct gas monitoring systems.

Reagents

HCl 6 N
Standard I_3^-, 0.025 N
Standard $S_2O_3^{2-}$ 0.025 N
Starch indicator
Standard $K_2Cr_2O_7$, 0.025 N for standardizing $S_2O_3^{2-}$
KI
Na_2CO_3

Equipment

Burets
Pipets
Magnetic stirrer and stir bars
Standard lab glassware

Procedure

Preparation and Standardization of $S_2O_3^{2-}$ (0.025 N)

Dissolve 6.25 g of $Na_2S_2O_3 \cdot 5H_2O$ in 500 ml of freshly boiled and cooled DI water in a 1-l volumetric flask. Add 0.1 g Na_2CO_3. Dilute to 1 l with freshly boiled and cooled DI water. Mix well and store in tightly closed glass bottle.

Dissolve an accurately weighed (~0.49 g) portion of dried primary standard $K_2Cr_2O_7$ in DI water in a 1-l volumetric flask. Dilute to mark, mix well, and store in any convenient container. Calculate normality of this solution by:

$$N_{Cr_2O_7^=} = \frac{\text{wt } K_2Cr_2O_7\text{(g)}}{\text{(49.03) (volume solution, l)}}$$

$N_{Cr_2O_7^=}$ should be approximately 0.01 N

To a glass-stoppered Erlenmeyer flask, add 20.0 ml of 0.01 N $K_2Cr_2O_7$ (by pipet), 3 ml of 6 N HCl, and ~3 g solid KI. Stopper the flask, swirl to ensure good mixing, and let stand in the dark for 10 min. After 10 min, add ~100 ml DI water, wash stopper and sides of flask with DI water. Titrate with 0.025 N $S_2O_3^=$ (10 ml buret) until the solution has only a faint yellow color. Add 2 droppers of starch indicator solution and continue titration to the disappearance of the blue color. Repeat this standardization procedure at least two more times.

Calculate normality of the $S_2O_3^=$ from individual titrations and use an average result.

$$N_{S_2O_3^=} = N_{Cr_2O_7^=} \times \frac{\text{Volume } Cr_2O_7^= \text{ solution taken (ml)}}{\text{Volume } S_2O_3^= \text{ solution used for titration (ml)}}$$

Preparation and Standardization of Iodine (I_3^-)

Dissolve 20 to 25 g KI in a partially filled 1-l volumetric flask. Add 3.2 g iodine and allow to dissolve. Dilute to 1 l. Store in an amber bottle or other container suitably shielded from light.

Pipet 5.00 ml of iodine solution into Erlenmeyer flask. Add ~100 ml DI water. Titrate with $S_2O_3^{2-}$ solution until a pale straw color is obtained. Add starch indicator as above and continue titration to the disappearance of blue color. Repeat this standardization titration at least two more times. Calculate normality of the iodine solution by:

$$N_{I_3^-} = N_{S_2O_3^=} \times \frac{\text{Volume } S_2O_3^= \text{ used for titration (ml)}}{\text{Volume } I_3^- \text{ solution taken (ml)}}$$

Titration of Sample

If the $Zn(OAc)_2$ preserved sample has a pH >6 adjust the pH to less than 6 and immediately add a known amount of standard iodine (I_3^-) solution. Than add (an additional) 2 ml 6 N HCl to fully dissolve any solids. If the iodine color disappears, immediately add more I_3^- solution until color is permanent. Record total volume of I_3^- added. Also, if precipitate is not completely dissolved, add more HCl. Titrate with standard thiosulfate until only a pale yellow color remains. Add 2 ml of starch indicator solution and continue titration to the disappearance of blue color.

Calculation

$$\text{mg } S^=/l = \frac{1.6 \times 10^4 (A-B)}{\text{ml sample}}$$

A = (ml of I3 solution used) x (normality I_3^- solution)
B = (ml of $S_2O_3^=$ solution used) x (normality $S_2O_3^=$ solution)

4.3 METALS AND METALLOID ELEMENT ANALYSES

Atomic Absorption

Atomic absorption spectroscopy is probably the most widely available and used method for trace metal analysis. Due to the general availability of AA instrumentation and the extensive documentation of interferences and problems, atomic absorption spectroscopy is the method of choice whenever applicable.

In order to obtain detection limits for some metals in the range necessary to ascertain conformity to aquatic life criteria standards (which represent the best analytical sensitivity required) several variants of straightforward flame AA need to be used. The first variant is flameless atomization, most often controlled by a graphite furnace attachment. Generally, very little sample handling is necessary (little potential contamination) and realizable detection limits are 2 or 3 orders of magnitude lower than with conventional flame AA.

In this document, analyses of Ag, Cd, Cr, Pb, and Zn are recommended to be performed by graphite furnace AA. For these elements, direct AA, without some preconcentration step, is not capable of detection at or near the currently specified levels for conformance to the aquatic life criteria.

For As and Se, hydride evolution followed by H_2/Ar flame AA is specified.

Chelation extraction can be used as a separation, preconcentration technique for many trace metals. Some interferences can be removed or reduced in this manner, and if the concentration is large enough, direct flame AA of the extract can realize the desired low detection limits. The sample handling steps involved in the extraction procedure are a potential source of contamination.

Cold vapor AA is the method of choice for Hg. No other simple and generally available technique can reach the necessary low detection limit.

Inductivity Coupled Argon Plasma-Atomic Emission Spectroscopy (ICP-AES)

ICP-AES is rapidly growing in popularity for simultaneously determining many trace metals concentrations. Generally, detection limits are comparable or lower than direct flame AA. ICP-AES instruments currently are more expensive than AA spectrometers, but the price gap is narrowing as more manufacturers enter the field. The simultaneous multielement capability of ICP-AES represents a tenfold or greater improvement in sample throughput and thus, in the long run, a smaller cost per sample compared with AA.

Chemical, physical, and spectral interferences are less well known for ICP-AES methodology than for AA, but this knowledge gap is decreasing as ICP-AES gains popularity and practitioners gain experience. As a general rule of thumb, elements that can be analyzed with sufficiently low detection limit by direct AA also can be analyzed by ICP-AES. For some elements addressed in this document, notably B and Al, ICP-AES is preferred to conventional flame AA. Other refractory oxide forming elements would also be more conveniently analyzed using ICP-AES.

Preconcentration prior to ICP-AES would be necessary to analyze many of the elements ordinarily handled by graphite furnace AA. The use of a nonselective chelant-extraction such as diethylammonium diethyldithiocarbamate (DeKhopkar and Chalmers 1970), coupled with ICP-AES, offers the attractive possibility of simultaneous isolation, concentration, and determination of trace metals contained in brine matrices. Presently, solvent extraction using diethylammonium diethyldithiocarbamate (DDTC) in $CHCl_3$ is being evaluated as a means of quantitatively extracting a suite of thiophilic metal ions from simulated brines. The thiophilic metals studied are: Ag, As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, Tl, and Zn. Briefly, the procedure consists of the following steps: First, brine sample (100 ml) is rendered acidic with HCl, treated with KI to reduce As (V) and Sb (V) to As (III) and Sb (III), and extracted twice with 1% DDTC in $CHCl_3$. Secondly, pH is adjusted to ~4.5 with NaOH and sodium acetate and extracted twice with the same DDTC in $CHCl_3$. Third, the combined extracts are evaporated to dryness, treated alternately with HNO_3 and H_2O_2 and finally diluted to 10.0 ml. The 10.0 ml solution is then subjected to ICP-AES analysis to assess recoveries. Preliminary unpublished studies without the initial HCl, KI treatment showed good recoveries for the elements studied except As and Sb. Investigation is continuing.

Matrix Matching of Standards and Spike Recovery

If spike recovery is less than ~95%, the presence of a matrix effects should be suspected. There are other possible causes for less than quantitative recovery but most can be ruled out by careful preparation of spiked samples. In cases of a matrix effect two general ways to obtain reliable analyses are: 1) use matrix-matched standards or 2) calculate results from standard addition data rather than direct comparison with a calibration curve. On the other hand, if spike recovery is quantitative (>95%), direct comparison with a calibration curve based on pure standards is acceptable.

Matrix-matched standards are recommended in this document primarily because the spike recovery experiment would not be needed and, hence, the decision regarding standard addition data, matrix-matched standards, or simple pure standards would not have to be made.

4.3.1 Aluminum

Method Title

Inductively Coupled Argon Plasma-Atomic Emission Spectroscopy

Method Summary

Sample is directly aspirated into nebulizer of precalibrated ICP-AES spectrometer. Emission intensity at 308.2 nm is measured and compared with matrix-matched standards.

Analytical Range

≥ 50 µg/l

Sample Size

10 ml

Precision

±10%

Published References

EPA Method 200.7 (1979)
Fed. Reg. 44, 69464 (12/3/79).

Potential Interferences and Comments

High concentrations of Mn or V represent potential spectral interferences. Mn at 100 ppm produces a signal equivalent to 0.21 ppm Al, and V at 100 ppm provides a signal equivalent to 1.4 ppm.

ICP-AES and graphite furnace AA are the only common techniques available to analyze soluble Al at levels expected in geothermal samples.

Alternative Analytical Method

1. Graphite furnace AA.
2. Solvent extraction using oxine in methyl-isobutylketone (MIBK) followed by direct aspiration into an atomic absorption spectrometer has been recommended by APHA, 14th Edition, p. 155-156 (1975).

Reagents

Al metal or a pure Al compound [e.g., $KAl(SO_4)_2 \cdot 12H_2O$] for preparing standards

HCl and/or HNO_3

Equipment

ICP - emission spectrometer with Al channel

Procedure

Aspirate sample and appropriate matrix-matched standards into ICP-AES nebulizer.

Calculation

Al content of sample is determined by comparing emission intensities observed for standards and samples.

4.3.2 Arsenic

Method Title

Atomic Absorption - Gaseous Hydride

Method Summary

Arsenic in the sample is first reduced to the trivalent form by using $SnCl_2$ and then converted to arsine, AsH_3, by using zinc metal or $NaBH_4$. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrometer.

Analytical Range	Sample Size
2-20 µg/l	25 ml

Precision	Published References
±10%	EPA, #206.3, 1974, NPDES and SDWA approved, Storet #01002 (total) #01000 (dissolved) #01001 (suspended) APHA 301A VII, p. 159-162 (1975)

Potential Interferences and Comments

Appreciable concentrations of several metals (Cr, Co, Cu, Hg, Mg, Ni, Ag) interfere, but normally would not be a problem in geothermal fluids.

Alternative Analytical Methods

1. Furnace atomic absorption is quoted to have a slightly higher detection limit (EPA PB297686, p. 69-70, 1979). High levels of Cl^- and SO_4^{2-} have been suggested as potential interferences. Matrix-matched standards are recommended along with rigorous washing (with HNO_3) of all labware used.

2. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) has been applied to the analysis of As in geothermal fluids. The analytical range is greater than with atomic absorption techniques, but detection limit is considerably higher, ~100 µg/l. Matrix matching of standards is highly recommended.

3. Various spectrophotometric analyses have been suggested. The most popular seems to be the method based on trapping arsine (from an arsine generator) in pyridine solution of silver diethyldithiocarbamate and measuring the absorbance at 535 nm. Detection limit for this method is quoted to be

similar to AA methods discussed above, and the same metals, if present, will interfere because of the common arsine generation step. Care must be taken to remove all H_2S from arsine gas stream through extensive sparging of the solution after addition of $SnCl_2$ and before addition of Zn or $NaBH_4$ because Ag_2S formation in trapping solution would cause turbidity. Finally, HNO_3 cannot be used as a preservative in solutions to be analyzed for As by arsine generation; negative interference has been observed.

Reagents

Arsenic standards (As_2O_3)
$SnCl_2$ solution (100 g/100 ml) conc HCl)
Zn (50 g of 200 mesh dust in 100 ml deionized water)
KI solution (20 g/100 ml)
H_2SO_4
HCl

Equipment

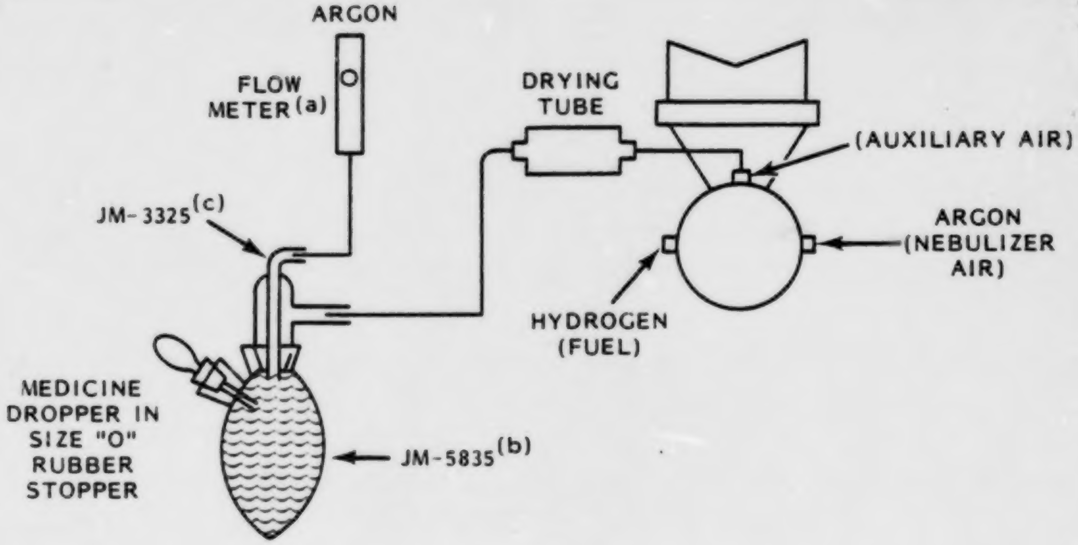
Atomic absorption spectrometer
Arsenic lamp (hollow cathode or electrodeless discharge
Hydride generation apparatus

Procedure

Apparatus setup: Connect the apparatus with the burner of the spectrophotometer as shown in Figure 4.2 Connect the outlet of the reaction vessel to the auxiliary oxidant input of the burner with Tygon tubing. Connect the inlet of the reaction vessel to the outlet side of the auxiliary oxidant (argon supply) control valve of the instrument.

Arsenic solutions:

1. Stock arsenic solution - Dissolve 1.3209 g arsenic trioxide, As_2O_3, in 100 ml distilled water containing 4 g NaOH, and dilute to 1000 ml with deionized distilled water; 1.00 ml = 1.00 mg As.
2. Intermediate arsenic solution - Pipet 1 ml stock arsenic solution into a 100-ml volumetric flask, and bring to volume with deionized distilled water containing 1.5 ml conc HCl/l; 1.00 ml = 10.0 μg As.
3. Standard arsenic solution - Pipet 10 ml intermediate arsenic solution into a 100-ml volumetric flask, and bring to volume with deionized distilled water containing 1.5 ml conc HCl/l; 1.00 ml = 1 μg As.


ARGON
FLOW METER(a)
DRYING TUBE
(AUXILIARY AIR)
JM-3325(c)
ARGON (NEBULIZER AIR)
HYDROGEN (FUEL)
MEDICINE DROPPER IN SIZE "O" RUBBER STOPPER
JM-5835(b)

a. CALMONT NO 12 OR EQUIVALENT

b. SCIENTIFIC GLASS JM 5835 OR EQUIVALENT

c. SCIENTIFIC GLASS JM 3325 OR EQUIVALENT

FIGURE 4.2. Schematic Arrangement of Equipment for Analyzing Arsenic (and Selenium)

Instrument operation: Because of differences between various models of atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. In general, proceed as follows.

1. Install an arsenic lamp in the instrument; set the wavelength dial to 193.7 nm; and align the lamp in accordance with the manufacturer's instructions.

2. Set the slit width according to the manufacturer's suggested setting for the element being measured.

3. Turn on the instrument and apply the amount of current to the lamp suggested by the manufacturer.

4. Allow the instrument to warm up; 10 to 20 min are usually required.

5. Install a Boling burner head.

6. Turn on the argon and adjust to a flow rate of about 8 l/min, with the auxiliary argon flow at 1 l/min.

7. Turn on the hydrogen, adjust to a flow rate of about 7 l/min, and ignite flame. The flame is essentially colorless. To determine whether the flame is ignited, pass the hand about 30 cm (1 ft) above the burner to detect the heat emitted.

8. Atomize the standard solution (1.00 ml = 1.00 μg) of arsenic, and adjust the burner both sideways and vertically in the light path until maximum response is obtained.

9. The instrument is now ready to run standards and samples by the arrangement of Figure 4.2.

Sample preparation - inorganic arsenic: To a 50-ml volumetric flask, add 25 ml sample, 20 ml conc HCl, and 5 ml 18 N H_2SO_4.

Preparation of standards: Transfer 0, 0.5, 1.0, 1.5, and 2.0 ml standard arsenic solution to 100-ml volumetric flasks and bring to volume with diluent(a) to obtain concentrations of 0, 5, 10, 15, and 20 μg/l arsenic.

Treatment of sample and standards: Transfer a 25-ml portion of sample or standard as prepared above to reaction vessel, and add 1 ml of KI solution. Next, add 0.5 ml $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill a medicine dropper with 1.50 ml zinc slurry that has been kept in suspension with a magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard. The metal hydride will produce a peak almost immediately. When the recorder pen returns part way to the baseline, remove the reaction vessel.

Calculation

Draw a standard curve by plotting peak heights of standards versus concentration of standards. Measure the peak heights of the samples and read the concentration from the curve. Multiply these concentrations by 2 since the sample was diluted 1 + 1 with acid.

(a) Recommended diluent consists of 100 ml 18 N H_2SO_4 + 400 ml conc HCl diluted to 1 l with deionized water.

4.3.3 Barium

Method Title

Atomic Absorption

Method Summary

The sample is directly aspirated into nitrous oxide-acetylene, fuel-rich flame of an atomic absorption spectrometer. Absorbance is measured at 553.6 nm and compared with matrix-matched standards.

Analytical Range

0.5-20 mg/l

Sample Size

$\geq$10 ml

Precision

$\geq$10%

Published References

EPA #208.1, 1974 NPDES and SDWA approved, Storet #01007 (total) #01005 (dissolved) #01006 (suspended)

APHA 14th Edition, p. 152-155 (1979)

Potential Interferences and Comments

Like other alkali and alkaline-earth elements, significant ionization of Ba occurs in the N_2O/C_2H_2 flame. Brine samples containing $\geq$1000 ppm alkalis (as K) supply their own ionization suppression of Ba. Standards should contain comparable concentrations of alkali elements. Use of N_2O/C_2H_2 flame virtually eliminates chemical interferences and is recommended.

If air/C_2H_2 flame is used aluminum, silica, and phosphate depress the Ba absorbance. This interference can be largely eliminated by addition of 2000 mg/l lanthanum.

Alternative Analytical Method

1. ICP-AES has been used successfully to analyze brine samples. Detection limit and precision are comparable to AA. To ensure accuracy and consistency, standards should be reasonably matrix matched, especially with respect to alkali elements.

2. Furnace AA can be used when Ba content of sample $\leq$200 μg/l.

Reagents

Ba standards
NaCl (for ionization suppression)
La salt for sample treatment if air/C_2H_2 flame used
C_2H_2, N_2O, air

Equipment

AA spectrometer
Ba hollow cathode lamp
N_2O burner head

Procedure

Adjust operating parameters of atomic absorption spectrometer according to instrument manufacturer's suggestions.

Preparation of Standard Solution

1. Stock solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to 1 l, 1 ml = 1 mg Ba (1000 mg/l).

2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 l.

3. Prepare dilutions of the stock barium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution. The calibration standards should be prepared to be as close to the sample in acid makeup and concentration as reasonably possible.

Calculation

Determine Ba content by direct comparison with standard curve. Correct result for reagent addition (NaCl or La^{3+}) as needed.

4.3.4 Boron

Method Title

Inductively Coupled Plasma-Optical Emission Spectroscopy

Method Summary

Boron-containing sample is nebulized into argon plasma. Radiation characteristic of boron at 249.77 nm is measured and compared with standards or, preferably, B-spiked samples.

Analytical Range	Sample Size
0.01-100 mg/l	5-10 ml

Precision	Published Reference
10%	EPA Method 200.7 (1979)

Potential Interferences

None of major significance known, round-robin tests (Kindle and Woodruff 1981; Karkalits and Hankins 1981) have shown this technique to yield good results in geothermal service.

Alternative Analytical Methods

1. The carminic acid colorimetric method for boron (ASTM D3082-74A) is currently one of the most popular methods among analysts in the geothermal area. Because nitrate ion severely interferes with this method, nitric acid preservation must be avoided. Fluoride, silicate, and phosphates are claimed to yield a slightly positive interference, but past geothermal use has shown good precision.

2. The azomethine-H (Sigma Chem Co. #A3144) colorimetric method has been shown to work well with steam samples (S. G. Sharp, Pacific Gas and Electric).

3. The curcumin colorimetric method is ranked less favorable than the carminic acid colorimetric method because of the many known interferences and higher detection limit.

4. Atomic absorption methods for boron have much higher detection limits than any of the methods discussed above and should utilize N_2O/C_2H_2 flames. Atomic absorption is not recommended for boron analysis.

Reagents	Equipment
Matrix-matched B standards HCl HNO_3	Inductively coupled plasma-atomic emission spectrometer with B channel

Procedure

A. Set up instrument with proper operating parameters as suggested by the instrument manufacturer's instructions. Initiate appropriate operating configuration of computer. Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using typical mixed calibration standards. Flush the system with the calibration blank (1 ml conc HNO_3 + 5 ml conc HCl diluted to 100 ml with deionized water) between each standard. For boron concentrations greater than 500 μg/l, extended flush times of 1 to 2 min may be required because of a "boron memory."

B. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

C. Begin the sample run, flushing the system with the calibration blank solution between each sample. Analyze the instrument check standard(a) and the calibration blank each 10 samples.

D. If the method of standard addition is used, the following procedure is recommended.

   1. The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift.

(a) The instrument check standard is prepared by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves.

2. The simplest version of the standard addition technique is the single-addition method.

   a. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the sample. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

   $$c_x \cong \frac{S_B V_s c_s}{(S_A - S_B)\, V_x}$$

   where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively.

   b. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

   c. For results from this technique to be valid, the following limitations must be taken into consideration:

      - The analytical curve must be linear.

      - The chemical form of the analyte added must respond the same as the analyte in the sample.

      - The interference effect must be constant over the working range of concern.

      - The signal must be corrected for any additive interference.

Calculation

Reagent blanks[a] should be subtracted from all samples. This step is particularly important for digested samples requiring large quantities of acids to complete the digestion.

If dilutions are performed, the appropriate factor must be applied to sample values.

Data should be rounded to the thousandth place, and all results should be reported in mg/l to three significant figures.

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[a] The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

4.3.5 Cadmium

Method Title

Atomic Absorption - Furnace Technique

Method Summary

A suitable aliquot (10 to 20 μl) is injected into the graphite furnace. Absorbance is measured at 228.8 nm by a Cd hollow cathode lamp source and a D_2 lamp background correction.

Analytical Range	Sample Size
0.5-10 μg/l	10-20 μl/injection

Precision	Published Reference
±5%	EPA #313.2, 1978 NPDES and SDWA approved Storet #01027 (total) #01025 (dissolved) #01026 (suspended)

Potential Interferences and Comments

The use of graphite furnace AA for cadmium analysis is extremely sensitive. Detection limit is reported to be less than 0.1 ppb for normal operating parameters. Extreme care in preparing of sampling and preservation containers, as well as all labware used, must be taken to avoid contamination at or near ppb levels of Cd. Carefully matrix-matched standards are recommended, especially with respect to alkali and alkaline-earth metals used to correct for broad-band, nonatomic absorption.

Alternative Analytical Methods

1. Direct aspiration of samples into air-acetylene flame, without extraction-concentration, can be used reliably if cadmium content $\geq$0.05 mg/l. However, current "aquatic life criteria and drinking water standards" quote an upper limit of 0.01 mg Cd/l, slightly below reliable range of direct aspiration analyses. Therefore, an extraction procedure is needed for samples with a Cd content close to 0.01 mg/l if direct AA is to be used.

2. Direct aspiration into ICP-AES instrument is useful for simultaneous multielement screening of samples for Cd. Detection limit is generally comparable to direct flame AA. Dithiocarbamate extraction

preceding aspiration into ICP is a very attractive alternative to recommended method, especially for the simultaneous analysis of "thiophilic" metals.

Reagents

Stock 2000 ppm Cd standard
40% $(NH_4)_2HPO_4$ solution
$$\left.\begin{array}{l}\mathrm{HNO_3}\\ \mathrm{NaCl}\\ \\ \mathrm{Ca\ salt}\end{array}\right\}\ \text{Cd free}$$

Equipment

Atomic absorption spectrophotometer
Cd hollow cathode lamp or Cd EDL
Graphite furnace attachment
D_2 background correction lamp

Procedure

Preparation of Standard Solution

1. Stock Solution: carefully weigh 2.282 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in DI water. 1 ml = 1 mg Cd (1000 mg/l).

2. Ammonium Phosphate Solution (40%): dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade), in DI water and dilute to 100 ml.

3. Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. Attempt to match alkali and alkaline-earth element concentrations of sample by use of NaCl and Ca^{2+}. To each 100 ml of standard and sample alike add 2.0 ml of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Analysis

Make replicate injections of standards and samples. Record analytical signal (peak height or area) for each injection. Construct a calibration curve from standards data. Make several injections of suitably "spiked" sample to verify the need for standard addition procedure (or lack of need). The use of matrix-matched standards is highly desirable, especially if spike recoveries are not close to 100%.

Calculation

Read Cd concentration directly from standard curve.

4.3.6. Chromium

Method Title

Atomic Absorption - Furnace Technique

Method Summary

Nitric acid preserved sample is treated with $Ca(NO_3)_2$ and H_2O_2. A suitable aliquot (10 to 20 μl) is injected into graphite furnace. Background corrected absorbance is measured at 357.9 nm and compared with similarly treated standards.

Analytical Range

5-100 μg/l

Sample Size

10-20 μl/injection

Precision

±5%

Published Reference

EPA #218.2, 1978 NPDES and SDWA approved
Storet #01034 (total) #01030 (dissolved)
#01031 (suspended)

Potential Interferences and Comments

In order to detect and quantify chromium content of samples in the range specified by current aquatic life criteria, only graphite furnace AA and some form of preconcentration (chelation extraction) followed by direct AA or ICP emission provide the necessary low detection limit.

N_2 should not be used as graphite furnace purge gas because of the likely formation of chromium nitrides and an adverse effect on accuracy.

Alternative Analytical Methods

1. Direct AA; N_2O/C_2H_2 (flame) following extraction is a suitable and appropriate method comparable to furnace AA. Procedures can be found in APHA p. 151-152 (1975).

2. The simultaneous extraction and determination of a multitude of trace metals by ICP-AES is a very attractive alternative method.

3. Various colorimetric methods for chromium lack the necessary low detection limits to perform analyses at the level required by aquatic life criteria. For this reason, colorimetric methods are not recommended.

Reagents

$Ca(NO_3)_2 \cdot 4H_2O$
H_2O_2
HNO_3
CrO_3 (for standards)

Equipment

Atomic absorption spectrophotometer
Cr hollow cathode lamp
Graphite furnace attachment
D_2 background correction lamp

Procedure

Set AA spectrometer controls and graphite furnace program as suggested by instrument manufacturer.

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 l with DI water. 1 ml = 1 mg Cr (1000 mg/l).

2. Calcium Nitrate Solution: Dissolve 11.8 g of $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in DI water and dilute to 100 ml. 1 ml = 20 mg Ca.

3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3. To each 100 ml of standard and sample alike, add 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution.

Sample Preparation

The nitric acid preserved sample should be treated with 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution per 100 ml sample.

Analysis Procedure

Make replicate injections of standards and samples. Record analytical signal (peak height or area) for each injection. Construct a calibration curve from standards data. Make several injections of suitably "spiked" sample to verify or omit need for standard addition procedure. The use of matrix-matched standards is highly desirable especially if spike recoveries are not close to 100%.

Calculation

Determine Cr content of sample by direct comparison to standard curve.

4.3.7 Copper

Method Title

Atomic Absorption

Method Summary

Samples containing Cu are aspirated directly into air acetylene flame. Absorbance of samples is compared with matrix-matched standards. Copper content is determined from calibration curve.

Analytical Range	Sample Size
0.1-4 mg/l	~10 ml

Precision	Published References
±5%	ASTM D1688D (1977) EPA #220.1, 1978 NPDES approved, Storet #01042 (total) #01040 (dissolved) #01041 (suspended)

Potential Interferences and Comments

Spectral interferences due to high Na and Ca levels in brines with low Cu content are compensated for by use of matrix-matched standards or by the standard addition technique.

Alternative Analytical Methods

1. For Cu contents in the low end of stated analytical range, i.e., 0.1 to 0.5 mg/l and below, the graphite furnace technique or some preconcentration step such as pyrrolidine dithiocarbamate extraction should be employed. Solvent extraction is particularly attractive because alkali and alkaline-earth elements are selectively left behind (ASTM D3558B, 1977).

2. ICP-AES has been used successfully for Cu in brines. The detection limit is quoted to be ~0.002 mg Cu/l and linear dynamic range up to ~100 mg/l. The minimal sample handling required (i.e., no preconcentration step) and the simultaneous multielement capability are very attractive features. Accuracy and precision are comparable to AA methods.

3. Several sensitive and selective spectrophotometric Cu analyses are ava lable. Most notable are the methods based on substituted 1, 10 phenanthroline reagents, e.g., 2,9-dimethy-1,10 phenanthroline, (neocuproine) (ASTM 308B, 1977). This method is claimed to be virtually interference-free except for large amounts of Cr and Sn, which would not be expected in geothermal fluids.

Reagents	Equipment
Cu AA standards	Atomic absorption spectrometer Cu HC lamp

Procedure

Adjust operating parameters of atomic absorption spectrometer according to instrument manufacturer's suggestions.

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of electrolytic copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 l with deionized distilled water. Final concentration is 1 mg Cu/ml (1000 mg/l).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same acid and to the same concentration as the sample. Attempts should be made to prepare calibration standards to contain nearly the same concentration of major elements as are present in the sample.

Calculation

Cu content of sample is determined by direct comparison to standard curve prepared from matrix-matched standards.

4.3.8 Lead

Method Title

Atomic Absorption - Furnace Technique

Method Summary

The sample containing Pb is treated with $La(NO_3)_3$. A suitable aliquot (10 to 20 μl) is injected into graphite furnace. Absorbance is measured at 283.3 nm with a Pb hollow cathode (HC) lamp source and D_2 lamp background correction.

Analytical Range

5-100 μg/l

Sample Size

10-20 μl/injection

Precision

±5-10%

Published Reference

EPA #239.2, 1978 NPDES and SDWA approved,
Storet #01051 (total)
#01049 (dissolved) #01050 (suspended)

Potential Interferences and Comments

Addition of La(III) to samples largely removes sulfate interference. Lead is ubiquitous, and utmost care to avoid inadvertent contamination is required. Ten percent HNO_3 + DI water rinsing of all labware (including disposable pipet tips) is highly recommended. The lead spectral line at 217.0 nm offers a lower detection limit but appears to give more erratic results.

Alternative Analytical Methods

1. Pyrrolidine dithiocarbamate in $CHCl_3$ or MIBK extractions of Pb and other thiophilic metals, coupled with direct aspiration into a conventional AA flame, has also been recommended (ASTM, D3559-B; and APHA 311A and references therein). The convenience of using flame AA rather than graphite furnace is largely negated by the extra procedural steps needed. Detection limits and precision are said to be comparable to the furnace technique.

2. ICP-AES and direct aspiration of samples into an AA flame are acceptable for geothermal fluids if sufficient Pb is present. As mentioned in (1) above, a chelating extraction step preceding ICP-AES analytical finish is an inviting possibility. The simultaneous multielement

capability of ICP-AES, coupled with simultaneous extraction-concentration of thiophilic heavy metals from background-enhancing alkali and alkaline-earth ions, promises to be a powerful combination.

3. Colorimetric, dithizone chelation and extraction of Pb is another possibility. However, even though the detection limit is well within the range expected for Pb in geothermal fluids, this method is not recommended. The multitude of steps required, the quantity of labware that must be HNO_3 washed and rinsed, and the large number of toxic/dangerous chemicals needed make this method unattractive.

Reagents

HNO_3
La_2O_3 or $La(NO_3)_3$
Pb standard [commercial or prepared from $Pb(NO_3)_2$]

Equipment

Atomic absorption spectrometer
Pb HC lamp or electrodeless discharge lamp
D_2 continuum background correction lamp

Procedure

Set AA spectrometer controls and graphite furnace program as suggested by instrument manufacturer.

Prepare standards from stock Pb in concentration range noted above. To each 100 ml of standard add 10 ml of 50 µg La/ml solution. Each standard should also be 1.0% (v/v) HNO_3. Treat sample identically. Standards should be prepared from stock at the time of analysis. Make replicate injections (10 or 20 µl each) of standards and sample. Record calibration curve from standards data. Make several injections of suitably "spiked" sample to verify or omit need for standard addition procedure.

Calculation

Pb content of sample is determined by direct comparison with calibration curve or calculated from standard addition data as appropriate.

4.3.9 Lithium

Method Title

Atomic Absorption

Method Summary

An aqueous sample, treated with ionization suppressor, is aspirated directly into air acetylene flame. Lithium is determined by comparison with matrix-matched (ionization suppressor) standards.

Analytical Range	Sample Size
0.05-2 mg/l	10 ml or more

Precision	Published Reference
±5%	ASTM D3561-77 (1977)

Potential Interferences and Comments

The main interference, due to ionization of Li in the flame, is readily circumvented by adding 1000 ppm of another easily ionized alkali element for suppression. In brine samples, enough Na^+ and K^+ are probably already present to serve the purpose. Standards must be treated with an alkali metal salt (e.g., NaCl) to match alkali metal content of sample.

Alternative Analytical Methods

1. Flame photometry (flame emission) has been used successfully. Precision, accuracy, linear working range, and detection limits are claimed to be comparable to AA. Use of ionization suppression is recommended here (APHA 312A, 1975).

2. ICP-AES has also been employed successfully for analyzing Li. This method has comparable precision, accuracy, and detection limit but also a much wider linear dynamic range (0.1 to 1000 mg/l). For brine samples, an ionization suppressor does not need to be added to sample, but standards should be closely matched in total alkali content. In many ways, e.g., speed, convenience, simultaneous multielement determinations, wider linear dynamic range, ICP-AES is superior to AA. However, at this time, more analysts probably have access to an AA spectrometer than ICP-AES; therefore, the flame AA method is chosen as the reference method.

Reagents

Li standard
NaCl or KCl for use as ionization suppressor

Equipment

Atomic absorption spectrometer
Li HC lamp

Procedure

Dilute samples, as needed, to achieve an Li concentration in the linear range of existing AA spectrometer (typically 0.05 to 2 mg/l). Make sure total alkali content of diluted sample = 1000 ppm (as K). Prepare a series of 3 or 4 standards with Li content in the same linear range and containing ~1000 ppm alkali (as K). Measure the absorbance of standards and sample by using instrument manufacturer's suggested parameters.

Calculation

Prepare a calibration curve from data generated with standards. Use the calibration curve to find Li content of diluted sample. Multiply ppm Li found by dilution factor used. Report: mg Li/l.

4.3.10 Manganese

Method Title

Atomic Absorption

Method Summary

Samples containing Mn are aspirated directly into an oxidizing air-acetylene flame. Background-corrected absorbance of samples measured at 279.5 nm is compared with that of matrix-matched calibration standards.

Analtyical Range	Sample Size
0.02-3 mg/l	~10 ml

Precision	Published Reference
±15-20%	EPA #243.1, 1978 NPDES approved, Storet #01055 (total) #01056 (dissolved) #01054 (suspended) ASTM D 858 B (1977)

Potential Interferences and Comments

Mg at levels $\geq$100 mg/l may interfere (ASTM). Chelation extraction can be used to separate Mn from major brine metal ions. For Mn, the efficiency of the usual pyrrolidine dithiocarbamate extraction is reputed to be highly pH dependent.

Alternative Analytical Methods

1. ICP-AES has been successfully used for Mn in brines: the detection limit is lower than direct flame AA, and the linear dynamic range is much greater than AA. Precision and accuracy generally are expected to be better than with AA. The simultaneous multielement capability of ICP-AES is a very attractive feature. Matrix-matched standards are recommended.

2. Colorimetric analysis of Mn based on the oxidation of Mn in sample to MnO_4^- is recommended for analysts who do not have access to AA or ICP. See ASTM D 858 A for details.

Reagents	Equipment
Matrix matched Mn standards	AA spectrometer Mn hollow cathode lamp D_2 background correction lamp

Procedure

Adjust operating parameters of atomic absorption spectrometer according to instrument manufacturer's suggestions.

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of manganese metal (analytical reagent grade) and dissolve in 10 ml of redistilled HNO_3. When solution is complete, dilute to 1 l with 1% (v/v) HCl. 1 ml = 1 mg Mn (1000 mg/l).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same acid and to the same concentration as the sample. Attempts should be made to prepare calibration standards to contain nearly the same concentration of major elements as are present in the sample.

Calculation

Mn content of sample is determined by direct comparison with standard curves prepared from matrix-matched standards.

4.3.11 Mercury

Method Title

Cold Vapor Atomic Absorption

Method Summary

The water sample (1 to 100 ml) is oxidized by adding potassium persulfate, potassium permanganate, and nitric acid (a good approach is to add these reagents in the field where they act as preservatives in properly cleaned glass bottles) and heating for 1 h at 80°C to decompose organic matter and convert organic forms of mercury to the Hg^{++} ion. The Hg is then reduced with stannous chloride, and the elemental Hg° vapor is swept through a mercury analyzer or a cell positioned in the light path of an atomic absorption spectrophotometer. The absorption of radiation at 253.7 nm by the mercury vapor is measured.

Analytical Range

10-20,000 ng/l

Sample Size

1-100 ml

Precision

±5-10%

Published References

EPA #245.1, 1974 NPDES approved,
Storet, #71900 (total)
#71890 (dissolved) #71895 (suspended)
APHA Method 303F, p. 164-166 (1980)

Potential Interferences and Comments

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water. Copper also has been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

Geothermal brines high in chlorides require additional permanganate. During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced with stannous chloride and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent. In addition, the dead air space in the reaction flask must be purged before the addition of stannous chloride. Both inorganic and organic mercury spikes have been quantitatively recovered from geothermal brines by using this technique.

Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present.

Reagents

Potassium persulfate - 5% w/v
Potassium permanganate - 5% w/v
Nitric acid (Hg free) - 16 M
Hydroxylamine hydrochloride - 12% w/v
Stannous chloride - 10% in 0.5 M H_2SO_4 w/v
Standard mercury solution - 10 mg/ml in 10% HNO_3 w/v containing 0.02% $K_2Cr_2O_7$ w/v

Equipment

LDC mercury monitor or
Coleman mercury analyzer or
Atomic absorption spectrophotometer with quartz window absorption cell in light path.

Procedure

Pipet 1 to 100 ml of sample into a 250-ml Erlenmeyer flask fitted with a 4-way stopcock. If the sample is less than 100 ml, make up the difference by adding the appropriate amount of Hg-free water. Add 2.5 ml conc HNO_3, 2.0 ml of 5% potassium persulfate, and 2.0 ml of 5% potassium permanganate. It is recommended that all of the above steps be performed in the field or as soon as possible after sampling. Stopper and heat in hot water bath at 80°C for 1 h. Cool, add 1.0 ml of 12% hydroxylamine hydrochloride and gently swirl to dissolve any MnO_2 that may have formed. Gently flush the dead air space of the flask with N_2 gas to purge out any Cl_2 gas that may have formed during the oxidation step. Add 10 ml of 10% $SnCl_2$, quickly attach the flask to the 4-way stopcock (in closed position) and wait 1 min. Then sweep Hg° vapor out of the flask at a flow rate of about 0.5 to 1 l/min through the Hg analyzer or absorption cell situated in the light beam of an atomic absorption spectrophotometer. A once-through or recirculating N_2 flow arrangement can be constructed. The absorbance will increase and reach a maximum value within about 30 s. Once the maximum value is reached, close the 4-way stopcock to the flask and continue purging the rest of the system with the N_2 flow through the bypass valve until the absorbance returns to its minimum value.

Standard additions of the standard mercury solution are prepared and handled in the same manner. A standard curve is constructed by plotting peak height versus nanograms of mercury.

Calculation

Mercury content of sample is determined by direct comparison with standard curve.

4.3.12 Molybdenum

Atomic Absorption

Method Summary

Sample is directly aspirated into N_2O/C_2H_2 fuel-rich flame of an atomic absorption spectrometer. Absorbance is measured at 313.3 nm and compared with matrix-matched standards.

Analytical Range	Sample Size
1-25 mg/l	$\geq$10 ml

Precision	Published References
±3%	EPA #246.1, 1978 NPDES approved, Storet #01062 (total) #01060 (dissolved) #01061 (suspended) ASTM D3372 (1977)

Potential Interferences and Comments

Interference due to Ca and other ions has been observed. This source of interference can be controlled by treating the sample and standards so that 1000 mg/l of a refractory metal ion, such as Al, are present in the solution aspirated. For samples with Mo content less than ~0.5 mg, an extraction preconcentration step or use of graphite furnace is necessary.

Alternative Analytical Method

1. ICP-AES can be used for sample containing Mo at 50 μg/l or greater.

2. Graphite furnace AA, as mentioned above, is applicable to samples containing 3 to 60 μg/l.

Reagents	Equipment
$(NH_4)_6Mo_7O_{24}.4H_2O$	Atomic absorption spectrophotometer Mo hollow cathode lamp N_2O burner head

Procedure

Set up atomic absorption spectrometer as suggested by instrument manufacturer's literature.

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.840 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 1 l. 1 ml = 1 mg Mo (1000 mg/l).
2. Aluminum Nitrate Solution: Dissolve 130 g aluminum nitrate, $Al(NO_3)_3\cdot9H_2O$, in 150 ml of deionized distilled water; heat to dissolve. Allow to cool and dilute to 200 ml.
3. Prepare dilutions of the stock molybdenum solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same acid and to the same concentration as the sample. To each 100 ml of standard and sample alike, add 2 ml of the aluminum nitrate solution.

Calculation

Mo content of sample is determined by comparing absorbances measured for identically treated standards and sample.

4.3.13 Selenium

Method Title

Atomic Absorption, Gaseous Hydride

Method Summary

The selenium in the sample is reduced to +4 oxidation state by addition of $SnCl_2$. Finely divided metallic zinc or $NaBH_4$ is added to the acidified sample, which produces H_2(g) and H_2Se. The evolved gases are swept into an argon-hydrogen flame of an atomic absorption spectrometer. Background-corrected absorbance at 196.0 nm is measured and compared with standards.

Analytical Range

2-20 μg/l

Sample Size

25 ml

Precision

~15%

Published References

EPA #270.3, 1974 NPDES and SDWA approved, Storet #01147 (total) #01145 (dissolved) #01146 (suspended)
APHA 301A VII, p. 159-162 (1975)

Potential Interferences and Comments

Cr, Co, Cu, Hg, Mo, Ni, or Ag, if present in concentrations comparable or higher than Se, are known to interfere.

Alternative Analytical Methods

1. Graphite furnace atomic absorption offers comparable detection limits and analytical range. However, chloride (>200 mg/l) interferes. By treating samples and standards with $Ni(NO_3)_2$, the sulfate interference can be largely overcome (EPA PB297686, p. 183-185, 1979).

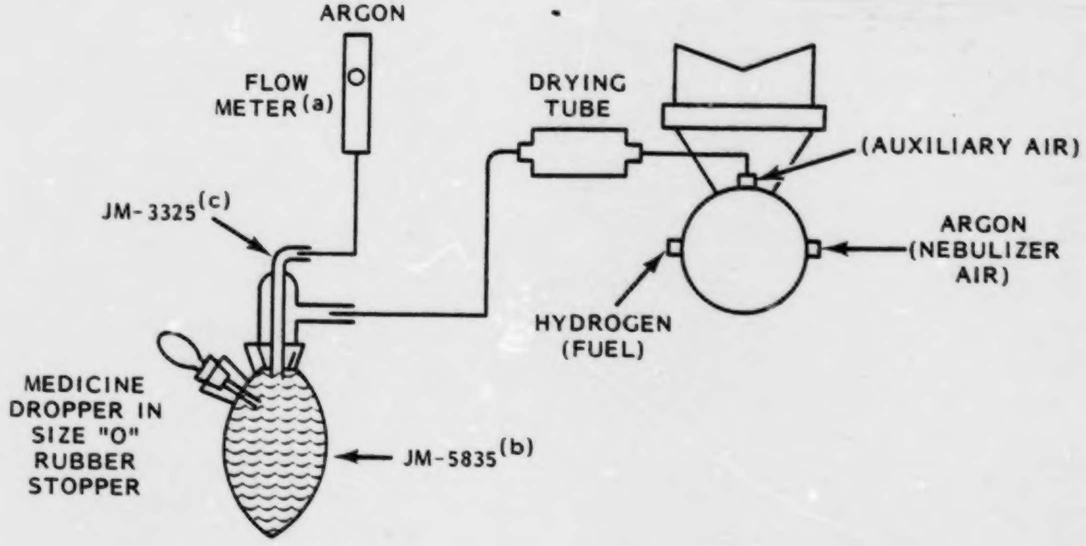
2. ICP-AES has been used and is applicable to samples containing >100 μg/l Se. Without a preconcentration step, ICP-AES is not recommended here if Se is to be measured in the range specified in "Aquatic Life Criteria and Drinking Water Standards."

3. Colorimetric (diaminobenzidine) method. See APHA, 14, p. 237-242 (1975). This method, claimed to be virtually interference free when preceded by a distillation step, is capable of ppb detection limit. The multitude of handling steps and reagents used is an unattractive feature.

Reagents	Equipment
Se	AA spectrometer
$SnCl_2$ solution (100 g/100 ml conc HCl)	Se lamp (HC or EDL)
Zn (50 g of 200-mesh dust in deionized water)	Hydride generation apparatus
H_2SO_4	
HCl	
HNO_3	

Procedure

1. Apparatus setup: Connect the apparatus with the burner of the spectrophotometer as shown in Figure 4.3. With Tygon tubing, connect the


ARGON
FLOW METER (a)
DRYING TUBE
(AUXILIARY AIR)
JM-3325 (c)
ARGON (NEBULIZER AIR)
HYDROGEN (FUEL)
MEDICINE DROPPER IN SIZE "O" RUBBER STOPPER
JM-5835 (b)

a. CALMONT NO 12 OR EQUIVALENT
b. SCIENTIFIC GLASS JM 5835 OR EQUIVALENT
c. SCIENTIFIC GLASS JM 3325 OR EQUIVALENT

FIGURE 4.3. Schematic Arrangement of Equipment for Analyzing Selenium (and Arsenic)

outlet of the reaction vessel to the auxiliary oxidant input of the burner. Connect the inlet of the reaction vessel to the outlet side of the auxiliary oxidant (argon supply) control valve of the instrument.

2. Selenium solutions:

   a. Stock selenium solution: Dissolve 100 g selenium in 5 ml conc HNO_3. Warm until the reaction is complete and cautiously evaporate just to dryness. Dilute to 1000 ml with deionized distilled water. 1.00 ml = 1.00 mg Se.

   b. Intermediate selenium solution: Pipet 1 ml stock selenium solution into a 100-ml volumetric flask and bring to volume with deionized distilled water containing 1.5 ml conc HNO_3/l. 1.0 ml = 10.0 μg Se.

   c. Standard selenium solution: Pipet 10 ml intermediate selenium solution into a 100-ml volumetric flask and bring to volume with deionized distilled water containing 1.5 ml conc HNO_3/l. 1.00 ml = 1.00 μg Se.

3. Instrument operation: Because of differences between makes and models of satisfactory atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. In general, proceed as follows:

   a. Install a selenium hollow cathode lamp or EDL of the desired metal in the instrument; set the wavelength dial to 196.0 nm; and align the lamp in accordance with the manufacturer's instructions.

   b. Set the slit width according to the manufacturer's suggested setting for the element being measured.

   c. Turn on the instrument and apply to the lamp the amount of current suggested by the manufacturer.

   d. Allow the instrument to warm up until the energy source stabilizes; this process usually requires 10 to 20 min.

   e. Install a Boling burner head.

   f. Turn on the argon and adjust to a flow rate of about 8 l/min, with the auxiliary argon flow at 1 l/min.

g. Turn on the hydrogen, adjust to a flow rate of about 7 l/min and ignite the flame. The flame is essentially colorless. To determine whether the flame is ignited, pass the hand about 30 cm (1 ft) above the burner to detect the heat emitted.

h. Atomize the standard solution (1.00 ml = 1.00 μg) of the desired metal, and adjust the burner both sideways and vertically in the light path until maximum response is obtained.

i. The instrument is now ready to run standards and samples by the arrangement of Figure 4.3.

4. Sample preparation - inorganic selenium: To a 50-ml volumetric flask, add 25 ml sample, 20 ml conc HCl, and 5 ml 18 N H_2SO_4.

5. Preparation of standards: Transfer 0, 0.5, 1.0, 1.5, and 2.0 ml standard selenium to 100-ml volumetric flasks and bring to volume with diluent(a) to obtain concentrations of 0, 5, 10, 15, and 20 μg/l Se.

6. Treatment of samples and standards: Transfer a 2-ml portion of sample or standard as prepared in Items 4 and 5 to reaction vessel of hydride generation apparatus. Add 0.5 ml $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill a medicine dropper with 1.50 ml zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard. The metal hydride will produce a peak almost immediately. When the recorder pen returns part way to the baseline, remove the reaction vessel.

Calculation

Draw a standard curve by plotting peak heights of standards versus concentration of standards. Measure the peak heights of the samples and read the concentration from the curve. Multiply these concentrations by 2 because the sample was diluted 1 + 1 with acid.

(a) Recommended diluent consists of 100 ml 18 N H_2SO_4 + 400 ml conc HCl diluted to 1 l with deionized water.

4.3.14 Silica (SiO_2)

Method Title

Molybdosilicate Colorimetric

Method Summary

A silica-containing sample is treated with molybdate ion in acid solution. Absorbance of complex formed is measured at 410 nm and compared with standards.

Analytical Range

2-25 mg SiO_2

Sample Size

50 ml

Precision

~10%

Published References

EPA #370.1, 1978 NPDES approved,
Storet # 00955 (dissolved)
ASTM D859C (1977)
APHA 426B (1975)

Potential Interferences and Comments

As in other colorimetric analyses, turbidity and color of sample can interfere. Iron and sulfide have been noted to interfere if present in concentrations comparable to or larger than SiO_2; however, this is not the case in geothermal brines. It is claimed that not all dissolved silica is reactive with the molybdate reagent (only the silica monomer is). A sodium bicarbonate digestion step (see one of references cited above) preceding color development reportedly converts all soluble silica to molybdate-active form; however, this step is not necessary if the sample is field diluted 10-fold as a preservative measure.

For silica concentrations less than ~2 mg/l, a working analytical range of ~0.1 to 2 mg/l can be realized by treating the molybdosilicate with a mild reducing agent to form "heteropoly molybdosilicate" (λ_{max} = 815 nm or 650 nm). For analyses to be made in this lower range, extra care is needed to avoid contamination; glassware should not be used.

For high salinity brines (Salton Sea geothermal fluids) the alternative methods will give somewhat better precision than the basic colorimetric method.

Alternative Analytical Method

1. ICP-AES is a very convenient alternative method of analysis.

2. Silicon can also be determined by direct AA using N_2O/C_2H_2 flame. Careful alignment of burner height is needed. B, F, and K at high concentrations (~1%) are known to depress absorption.

Reagents

$NaHCO_3$
H_2SO_4
HCl
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
NH_4OH
$Na_2SiO_3 \cdot 9H_2O$
$H_2C_2O_4 \cdot 2H_2O$
$(NaHSO_3)$[a]
(Na_2SO_3)[a]
(1-amino-2-naphthol-4-sulfonic acid)[a]

Equipment

Spectrophotometer or colorimeter
Pt dishes for use in digestion step
Nessler tubes

Procedure

Preparation of Reagent Solutions

Ammonium molybdate reagent: Place 10 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in distilled water in a 100-ml volumetric flask. Dissolve by stirring and gently warming. Dilute to the mark. Filter if necessary. Adjust to pH 7 or 8 with silica-free NH_4OH or NaOH. Store in plastic bottle.

Oxalic acid solution: Dissolve 10 g $H_2C_2O_4 \cdot 2H_2O$ in distilled water in a 100-ml volumetric flask. Dilute to the mark. Store in plastic.

Reducing agent: Dissolve 500 mg of 1-amino-2-naphthol-4-sulfonic acid and 1 g Na_2SO_3 in 50 ml distilled water with gentle warming if necessary. Dissolve 30 g $NaHSO_3$ in 150 ml distilled water. Mix these two solutions. Filter into a plastic bottle. Refrigerate and avoid exposure to light. Discard when it darkens. If there is incomplete solubility or immediate darkening of the aminonaphthosulfonic acid solution do not use.

1 + 1 HCl and 1 N H_2SO_4 also required.

Preparation of Stock and Standard Silica Solutions

Stock silica solution: Dissolve 4.73 g sodium metasilicate nonahydrate, $Na_2SiO_3 \cdot 9H_2O$, in recently boiled and cooled distilled water. Dilute to approximately 900 ml. Analyze 100.0-ml portions by gravimetry. Adjust concentration to 1.000 mg/l SiO_2. Store in tightly sealed plastic bottle.

---

[a] for low concentration analytical option

Standard silica solution: Dilute 10.0 ml stock solution to 1 l with recently boiled and cooled distilled water. This is 10 mg/l SiO_2. (1.00 ml = 10.0 μg SiO_2). Store in tightly sealed plastic bottle.

1. Digestion: If molybdate unreactive silica is present and its inclusion in the analysis is desired, include this step, otherwise proceed to Step 2.
   a. Place 50 ml, or a smaller portion diluted to 50 ml, of sample in a 100-ml platinum dish.
   b. Add 200 mg silica-free $NaHCO_3$ and digest on a steam bath for 1 h. Cool.
   c. Add slowly and with stirring 2.4 ml H_2SO_4 (1 N).
   d. Immediately transfer to a 50-ml Nessler tube, dilute to the mark with distilled water and proceed to Step 2 without delay.
2. Color development
   a. Place 50 ml sample in a Nessler tube.
   b. Add rapidly 1.0 ml 1 + 1 HCl and 2.0 ml ammonium molybdate reagent.
   c. Mix by inverting at least 6 times.
   d. Let stand 5 to 10 min.
   e. Add 1.5 ml oxalic acid solution and mix thoroughly.
   f. Read color (spectrophotometrically or visually) after 2 min but within 15 min from the addition of oxalic acid.

Preparation of Standards

If digestion was used add 200 mg $NaHCO_3$ and 2.4 ml H_2SO_4 (1 N) to standards to compensate for silica introduced by these reagents and for effect of the salt on the color intensity.

Photometric Measurement

Prepare a calibration curve by using approximately six standards to span the range shown below with the selected light path.

Selection of Light Path Length for Various Silica Concentrations

Light Path (cm)	Silica in 54.5 ml Final Volume (μg)
1	200 to 1300
2	100 to 700
5	40 to 250
10	20 to 130

Carry out Step 2 above using distilled water as the reference. Read a blank.

Plot photometric reading *versus* μg of silica in the final solution of 54.5 ml. Run a reagent blank and at least one standard with each group of samples.

Correction for Color or Turbidity

A special blank is run using a portion of the sample and carrying out the procedure in Step 1, if used, and Step 2 except for the addition of ammonium molybdate.

Zero the photometer with this blank before reading the samples.

Procedure for Low Concentration (<100 μg/l)

1. Perform digestion Step 1 if needed.

2. Place 50 ml sample in a Nessler tube.

3. In rapid succession add 1.0 ml of 1 + 1 HCl.

4. Add 2.0 ml ammonium molybdate reagent.

5. Mix by inverting at least six times.

6. Let stand 5 to 10 min.

7. Add 1.5 ml oxalic acid solution.

8. Mix thoroughly.

9. At least 2, but not more than 15 min after oxalic acid addition, add 2.0 ml reducing agent.

10. Mix thoroughly.

11. Wait 5 min; read photometrically or visually.

12. If digestion was used, treat standards with $NaHCO_3$ and H_2SO_4 as suggested in "Preparation of Standards" section above.

Photometric Measurement

Prepare a calibration curve by using approximately six standards and a reagent blank to span the range shown below with the selected light path.

Selection of Light Path Length for
Various Silica Concentrations

Light Path (cm)	Silica in 56.5 ml Final Volume (μg) 650 nm	815 mn
1	40 to 300	20 to 100
2	20 to 150	10 to 50
5	7 to 50	4 to 20
10	4 to 30	2 to 10

Read versus distilled water.

Plot photometric reading at 650 nm or at 815 nm versus μg of silica in 56.5 ml.

For turbidity correction, treat a portion of sample with all reagents as above, omitting the ammonium molybdate and reducing agent.

Run a reagent blank and at least one standard (to check calibration curve drift) with each group of samples.

Calculation

Read μg SiO_2 from calibration curve or by visual comparison.

$$\text{mg/l } SiO_2 = \frac{\mu g SiO_2}{\text{ml sample}}$$

Report whether $NaHCO_3$ digestion was used.

4.3.15 Silver

Method Title

Atomic Absorption - Furnace Technique

Method Summary

Suitable aliquot (10 to 20 µl) of acid preserved sample is injected into graphite furnace. Absorbance is measured at 328.1 nm and compared with absorbance measured for freshly prepared matrix-matched standards.

Analytical Range

1-25 µg/l

Sample Size

20 µl/injection

Precision

±5%

Published Reference

EPA #272.2, 1978 NPDES and SDWA approved, Storet #01077 (total) #01075 (dissolved) #01076 (suspended)

Potential Interference and Comments

Without a preconcentration step, only graphite furnace AA (of all the commonly available analytical techniques) can reliably quantify silver at levels of 10 µg/l, the level required to conform to aquatic life criteria. Many geothermal brines may contain silver at significantly higher levels, perhaps allowing measurement by one of the alternative methods.

Alternative Analytical Method

1. Preconcentration by chelation extraction (dithizone or dithiocarbamate) followed by direct AA or ICP-AES can be used for silver analyses. This probably is the best method for concentrated brines to avoid overestimating Ag due to interferences if matrix-matched standards are not used.

2. Simple colorimetric methods for silver lack the required low detection limits needed to analyze silver at the 10-µg/l level. The complex procedure given in APHA 319B (1975) requiring several extractions and extreme care does have a detection limit of ~2ppb, but is not recommended because of its complexity and many interferences.

Reagents

$AgNO_3$ (for preparing standards)
HNO_3

Equipment

Atomic absorption spectrophotometer
Ag hollow cathode lamp
Graphite furnace attachment

Procedure

Set AA spectrometer controls and graphite furnace program as suggested by instrument manufacturer.

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 ml conc HNO_3 and make up to 1 l. 1 ml = 1 mg Ag (1000 mg/l).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using nitric acid and to the same concentration as the sample.

Analysis

Make replicate injections of standards and samples. Record analytical signal (peak height or area) for each injection. Construct a calibration curve from standards data. Make several injections of suitably "spiked" sample to verify or omit need for standard addition procedure. The use of matrix-matched standards is highly desirable, especially if spike recoveries are not close to 100%.

Calculation

Determine Ag content of sample by direct comparison with standard curve.

4.3.16 Zinc

Method Title

Atomic Absorption - Furnace Technique

Method Summary

A suitable aliquot (10 to 20 µl) is injected into graphite furnace. Absorbance is measured at 213.9 nm using a Zn hollow cathode lamp source and D_2 lamp background correction.

Analytical Range

0.2-4 µg/l

Sample Size

20 µl/injection

Precision

±10%

Published Reference

EPA #289.2, 1978 NPDES approved,
Storet #01092 (total)
#01090 (dissolved) #01091 (suspended)

Potential Interferences and Comments

The use of graphite furnace AA for zinc analysis is extremely sensitive. Detection limit is reported to be less than 0.1 ppb for normal operating parameters. Extreme care in preparing sampling and preservation containers, as well as all labware used, must be exercised to avoid contamination at or near ppb levels of Zn. Carefully matrix-matched standards are recommended, especially with respect to alkali and alkaline-earth metals to correct for broadband, nonatomic absorption.

Alternative Analytical Methods

1. Direct aspiration of samples into air-acetylene flame, without extraction-concentration, can be reliably used if zinc content $\geq$0.05 mg/l. However, current "aquatic life criteria and drinking water standards" quote an upper limit of 0.01 mg/l Zn, slightly below reliable range of direct aspiration analysis. Therefore, an extraction procedure is needed for samples with a Zn content close to 0.01 mg if direct AA is to be used.

2. Direct aspiration into ICP-AES instrument is useful for simultaneous multielement screening of samples for Zn. Detection limit is generally comparable to direct flame AA. Dithiocarbamate extraction preceding aspiration into ICP is a very attractive alternative to recommended method, especially for the simultaneous analysis of "thiophilic" metals.

Reagents

1 mg Zn/ml stock standard
Zn-free NaCl(a)
Zn-free Ca salt(a)

Equipment

Atomic absorption spectrophotometer
Zn hollow cathode lamp or Zn EDL
D_2 background correction lamp
Graphite furnace attachment

Procedure

Set AA spectrometer controls and graphite furnace program as suggested by instrument manufacturer.

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 ml HNO_3. When solution is complete dilute up to 1 l with deionized distilled water. 1 ml = 1 mg Zn (1000 mg/l).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and to the same concentration as the sample. Calibration standards should also contain sodium and calcium at approximately the same concentrations as in sample.

Analysis

Make replicate injections of standards and samples. Record analytical signal (peak height or area) for each injection. Construct a calibration curve from standards data. Make several injections of suitably "spiked" sample to verify the need (or lack thereof) for standard addition procedure. The use of matrix-matched standards is highly desirable, especially if spike recoveries are not close to 100%.

Calculation

Read Zn concentration directly from standard curve obtained with matrix-matched standards.

(a) For use in preparing matrix-matched working standards.

4.4 GASEOUS SAMPLES

4.4.1 Radon

Method Title

Lucas Counter

Method Summary

A noncondensable gas sample is introduced into a pre-evacuated Lucas tube. After a suitable time delay, the sample is counted for alpha (α) activity.

Procedure

Samples of the noncondensable gases are passed through a 0.4-μm Millipore filter and allowed to fill a pre-evacuated Lucas counter. The Lucas counter is filled to about 2 psig of gas from the pressurized condenser. After disconnecting the counter from the gas source, it is immediately opened to the ambient environment in order to equilibrate at the known measured atmospheric pressure shown on the manometer. This step is accomplished by opening and then closing the stopcock on the counter. The counter is then moved into a light-tight appliance where it is optically coupled to a photomultiplier tube. The alpha particle decay of radon is detected and counted by a portable single-channel scintillation spectrometer. Sample counting is performed about 4 h after sample extraction to allow equilibration of the radon daughter radionuclides (see Figure 2.15). Simultaneous pressure and temperature measurements are necessary in making final corrections to the calibrated volume of the Lucas tube contents.

Analytical Sensivity

>4 x 10^{-10} Ci/l

Sample Size

0.1 l

Precision

±5%

Published Reference

H. F. Lucas (1957)

Potential Interferences and Comments

Provided the particulate radon daughters and other naturally radioactive particulates have been filtered out, this method is free of interferences. When improved sensitivity is desired, large volume samples may be processed through cooled charcoal traps wherein the radon accumulates and is subsequently eluted into the Lucas counter. Sensitivity as high as 1 x 10^{-16} Ci/l has been reported using this technique.

Equipment

Lucas tube(s)
Scintillation Spectrometer

Calculations

The gas sample is collected in a known-volume Lucas counter. If needed, the Lucas counter volume can be determined by using standard displacement techniques. Volume corrections are made based upon the sampling conditions of temperature and pressure utilizing the ideal gas laws:

$$\frac{P_o V_o}{T_o} = \frac{P_x V_x}{T_x}$$

where $P_o V_o$ and T_o are standard conditions and $P_x V_x$ and T_x are actual sampling conditions.

The standard condition volume = V_o and

$$V_o = \frac{P_x V_x T_o}{P_o T_x}$$

The counting data given in counts/min (c/m) are then corrected for the radioactive decay time between sample equilibration time (4 h after collection) and the actual time of sample measurement. The basis of this correction is the 3.83-day half-life of the isotope, ^{222}Rn.

The counting activity, A, measured at some time after collection is related to the actual amount of activity, A_o, observed 4 hr after collection by the following:

$A = A_o e^{-0.181t}$ where t is the time in days following collection. Each Lucas tube is calibrated by the manufacturer for response to radon. The typical response of a 0.1-l tube is 5 c/m per 1 x 10^{-9} Ci of radon. The results are then expressed as total Ci/l of radon.

4.4.2 CO_2-Organic Gases, Other Noncondensable Gases

Method Title

Gas Chromatography - Mass Spectroscopy

Method Summary

Noncondensable gas samples preserved in Teflon®-lined stainless steel container are subjected to GC-MS analysis.

Analytical Range

>1 ppmv, variable

Sample Size

1 l

Precision

~5%

Published Reference

J. D. Ludwick et al. (1982)

Potential Interferences and Comments

None.

Alternative Analytical Methods

In some situations, use of GC alone may be satisfactory.

An alternative method for CO_2 is to trap the CO_2 in ~2N NaOH (using a scrubber bottle, Figure 3.1) and acid titrating the end points between pH 8.3 (HCO_3^-) and pH 4.5 (CO_2) as described in ASTM D513 (1977).

Reagents

GC or GC-MS calibration standards

Equipment

Gas chromatograph interfaced to mass spectrometer

4.4.3 Ammonia - Gas Phase

Method Title

Chemiluminescence from NO + O_3 reaction following oxidation of NH_3 to NO. Continuous monitoring.

Method Summary

Real-time, continuous measurements are made of the NO/NO_x concentrations in air by use of a chemiluminescence technique that takes advantage of the light emitted by the following reaction sequence:

$$NO + O_3 \longrightarrow NO_2^*$$
$$NO_2^* \longrightarrow NO_2 + h\nu$$

The intensity of the emission is proportional to the concentration of NO_2 produced. The light is detected by a photomultiplier tube, and the resultant current measured in electronic circuitry.

Differentiation of nitrogen species is accomplished by first passing the incoming air sample directly into the ozone reaction chamber for conversion and measurement, then alternately into a NO_2 to NO high-temperature converter for NO_2 measurement. In this same way, NH_3 is distinguished from NO/NO_x by the oxidation step needed to provide nitrogen oxides for instrumental response from the NH_3 gas.

Analytical Range

>1 ppbv

Sample Size

Continuous monitoring

Precision

±20% at 1 ppb
±2% at 1 ppm

Published Reference

Federal Register, Vol. 38, No. 110, "Tentative Method for the Continuous Measurement of NO_2 (Chemiluninescent)" Addenda C June 8, 1973

Potential Interferences and Comments

SO_2 has been noted as an interference.

Alternative Analytical Methods

Selective ion electrode following trapping in acid sparge (H_2SO_4) through which a known volume of gas is passed.

Equipment

Chemiluminescence Instrument

Procedure

Follow instrument manufacturer's suggested procedure for calibration and analysis.

4.4.4 Mercury

Method Title

Cold Vapor Atomic Absorption Spectroscopy

Method Summary

Gaseous samples from wells, power plant piping, cooling towers, or ambient atmosphere are drawn through a series of mercury absorbing tubular traps. The trap tubes are subsequently heated to liberate the absorbed Hg which is determined by a cold vapor AA instrument.

Analytical Range

>1 ng/l

Sample Size

0.1-10 l

Precision

±20%

Published References

R. W. Braman and D. L. Johnson (1974)
D. E. Robertson et al. (1977)

Potential Interferences and Comments

Interferences are not normally observed using this technique. Samples of geothermal noncondensable gases have occasionally contained mercury concentrations in excess of instrumental capabilities. Special, small sample aliquots are taken for measurement in these situations.

Alternative Analytical Methods

Gaseous samples can be sparged through a strong oxidizing solution (HNO_3, $KMnO_4$, $K_2S_2O_8$) to trap and preserve Hg. Final analytical work up procedure is described in Section 3.0. Analysis is also by cold vapor AA.

Equipment

Cold vapor atomic absorption spectrometer (e.g., Coleman, Model MAS-50)
Quartz-trapping tubes (Figure 2.15) containing

1) Chromasorb-W pretreated with 3% SE-30 silicone and HCl gas.
2) Chromasorb-W pretreated with NaOH
3) Silver-coated glass beads
4) Gold-coated glass beads.

Procedure

The gas is first flowed through a fiberglass filter to remove any microparticulate mercury and then through a quartz tube containing chromasorb-W which has been pretreated with 3% SE-30 silicone and HCl gas. This tube selectively removes Hg^{++} compounds and passes all other forms. The remaining gases then flow through a tube containing chromasorb-W which has been pretreated with NaOH. This adsorbent selectively removes methyl mercury. The gases are directed through a tube containing silver-coated glass beads to selectively remove elemental Hg° vapor, and finally through a tube filled with gold-coated glass beads. The gold absorbs all forms of mercury and here will pick up dimethyl mercury which passes through the first three tubes.

The tubes are then heated to desorb the mercury into a field-adapted, cold vapor atomic absorption spectrometer (Coleman, Model MAS-50) for immediate analysis. If these samples are to be preserved for later analysis the tubes are capped and kept cool for analysis at the earliest opportunity. Routine field standardization of the spectrometer is accomplished by introducing calibrated mercury vapor volumes into the instrumentation from a sealed glass bottle containing a drop of mercury at a known temperature. The chemical forms of the mercury vapor are measured after the manner of Robertson et al. (1977).

Calculation

Direct comparison with above mentioned known mercury vapor volumes.

4.4.5 Hydrogen Sulfide and Sulfur Dioxide

Method Title

Ambient Monitoring - Flame Photometric Detector

Method Summary

Airborne sulfur-containing compounds are determined by measuring the sulfur emission produced in a reducing hydrogen flame.

$$2H + S_2 \longrightarrow S_2^* + H_2$$

$$S_2^* \longrightarrow S_2 + h\nu \text{ (394 nm)}$$

The intensity of the emission is proportional to sulfur concentration. The light is detected by a photomultiplier tube, and the resultant current measured in electronic circuitry. Instrumental calibration is accomplished using NBS certified permeation tubes. Sample air is drawn into the instrument through a Teflon® probe by means of a vacuum pump. Particulate materials may be filtered as needed. The air passes through either an H_2S or SO_2 scrubber in order to make unique species measurements.

Analytical Range

>1 ppbv

Sample Size

Continuous monitoring

Precision

±20% at 1 ppb
±20% at 1 ppm

Published Reference

Reference or Equivalent Methods 40 CFR 53
Federal Register, Vol. 40, p. 7049,
Feb. 18, 1975 Amended, May 10, 1979, 44FR, 27571

Potential Interferences and Comments

CO_2 concentrations significantly above those found in ambient air quench the light emission from the excited sulfur species.

Alternative Analytical Methods

The recently developed photoionization detector for sulfur-containing compounds is capable of comparable sensitivity and detection limit.

Equipment

Flame/photometric detector (Meloy Model SA 285E or equivalent)
Permeation tube(s) for calibration

Procedure

Follow directions supplied by instrument manufacturer (Meloy Instruments, Springfield, Virginia, or equivalent).

Calibration

None required; instrument is direct reading.

4.4.6 Hydrogen Sulfide

Method Title

Wells and Power Plant Piping; Cooling Towers

Method Summary

As a primary aid to the sample quality, the gas stream can be continuously measured with an H_2S analyzer. Two types of the H_2S analyzer can be used for monitoring purposes: the gas amperometric device (Interscan Corp. Chatsworth, California, Model 1176) (or equivalent) and the lead acetate, colorimetric device (Houston Atlas Co. Houston, Texas, Model 825) (or equivalent). Where interferences are at a minimum the convenient amperometric instrument is preferred; however, where possible interferences are present, the colorimetric device has a response that is specific to H_2S. Quantitative measurements are made only after H_2S values climb and stabilize. Several real-time analysis intervals of 10 to 30 min are usually employed for the H_2S measurements.

Commercially available standardized H_2S gas sources are passed through a dilution system in a manner similar to actual sample handling, and then into the H_2S analyzer. Primary calibration of the standard H_2S can be accomplished using a Meloy Model 285 flame photometric sulfur analyzer (or equivalent) (method 4.4.5). This instrument is calibrated using a National Bureau of Standards (NBS) certified SO_2 permeation tube. In this way the exact H_2S concentration can be determined for all standard gas cylinders used as field standards. Once calibrated in this manner, no significant change in concentration has been noted in the cylinders for up to 12 months of field use. However, differences are often noted between the manufacturer's certification values and the secondary NBS calibration data, the severity of which varied with the material source.

Cooling tower exhaust concentrations of H_2S are within the range of amperometric monitoring instrumentation and no sampling dilution equipment is needed. The dilution equipment referred to is commercially available from the instrument manufacturers (Meloy and others) and will typically dilute the sample stream 1:1000 or by some other large factor.

Analytical Sensitivity	Sample Size
1 ppm (by volume)	Continuous Monitoring
Precision	**Published Reference**
5%	J. D. Ludwick et al. (1982)

Potential Interferences

None usually present in wells and power plant piping. High concentrations of CO, where present, produce instrumental responses of about 5% of that from H_2S in potentiometric equipment.

Alternative Analytical Methods

An alternative method utilizing pulsed fluorescence instrumental analysis is also acceptable.

Equipment

Flame/photometric detector (Meloy Model SA 285E or equivalent)

Procedure

Follow directions supplied by instrument manufacturer.

Calibration

Permeation tubes(s) and associated dilution equipment for calibration.

4.5 REFERENCES

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5.0 GROUNDWATER MONITORING

Flow of liquids in the subsurface occurs as either saturated or partially saturated flow. Monitoring of these distinct regimes requires special techniques and knowledge for each zone. This section gives design considerations and methods for collecting liquid samples from both the saturated and partially saturated zones. It briefly describes items such as well location and well construction to provide information that a project manager might use to discuss the options with a hydrologist or a drilling contractor. It would be wise to have a groundwater hydrologist review the local site since optimal well location is site specific.

Federal and State laws may require monitoring of either or both regimes (U.S. Dept. Interior 1981). The U.S. Environmental Protection Agency (EPA) criteria and standards for the Underground Injection Control (UIC) program are listed and updated in the Federal Register[a]. The Environmental Reporter publication and Code of Federal Regulations are also sources of rules and regulations. As of February 3, 1982, there are no specific regulations regarding injection wells used for geothermal plant effluent disposal. Class V wells are primarily inventory and assessment requirements (see Subpart F or 40 CFR 146 in the Appendix). The owner/operator must notify the Regional/Administrator or State Director of the existence of such wells and submit certain inventory information required by law [see Appendix for 40 CFR 122.37(c)] to enable the Director to report to EPA on construction features, nature and volume of injected fluids, contamination potential (using hydrogeological data available to the State), corrective alternatives, and recommendations for appropriate regulatory approaches and remedial actions.

State programs must be approved by EPA for participation in the permit programs. The State Director, therefore, should be contacted for detailed regulations and time specifications.

The description of various monitoring techniques in this section does not constitute recommendations relating to a legal requirement to perform groundwater monitoring.

5.1 PARTIALLY SATURATED ZONE

Water samples from the partially saturated portions of the vadose zone can be collected via two methods. The vadose zone is the subsurface zone between land surface and the permanent water table. It contains unsaturated material but may also contain temporary "layers" of saturated subsurface water as perched water tables. The two methods are as follows:

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[a] June 24, 1980, p. 42472 and February 3, 1982 p. 4992.

1. Direct sampling of the soil, followed by soil-water extraction and analysis.

   Soil samples are easily obtained by standard techniques during the drilling of a hole. Extracting the soil water and soil-water analysis are more complex, but valid results can still be obtained. The largest drawback to this method is that it is nonrepeatable for a given point. Special equipment is needed for each sampling period. Soil sampling is detailed in Section 5.4.1.

2. Installing a pressure-vacuum lysimeter.

   The use of a pressure-vacuum lysimeter requires that a borehole, similar to a well, be installed. The lysimeter system is installed and the hole backfilled in a specific manner. Water samples may then be collected by a partial vacuum being created in the lysimeter. Repeat samples can be collected at any specified interval. Lysimeters are discussed in Section 5.4.2.

5.2 SATURATED ZONE

Wells in the saturated zone can be classified into two general categories: 1) production and 2) observation/monitoring.

5.2.1 Production Wells

At any geothermal site, the initial wells probably will be the production (exploration) type. Production wells will be used to test the various resource zones and to assess site geology. Those wells, while not constructed for monitoring purposes, also can be used to determime water quality in their respective completion zones. Detailed hydrogeologic logs maintained during exploratory drilling can define shallow potable water resources that may be affected by geothermal development. Any existing domestic, irrigation, or public/industrial supply well in the vicinity may be used to obtain hydrologic and chemical data on local groundwater flow systems. Special wells may have to be drilled to adequately monitor for any contamination caused by resource development, depending on local requirements.

5.2.2 Monitoring Wells

Construction

To monitor a thick aquifer system, wells should be constructed so that they are open only to the target aquifer to be sampled. Where multiple aquifers are present, individual wells must be placed into each aquifer, or separate multiple completions must be provided for using advanced techniques. Monitoring wells should be screened over a minimum of 75% of the target aquifer thickness. Casing should extend from the top of the screen to the surface.

Well Diameter. The purpose of a monitoring well is to provide an access point for sampling water for a stratum of interest. The well diameter must be large enough to accommodate the sampling equipment. Depth to water, volume of the well, volume of sample, and the analysis parameters must be considered so that the sampling device chosen is compatible with the well size.

Casing Material. Most monitoring wells are now cased with PVC. PVC casing is low cost, light weight, and relatively resistant to most corrosive substances. Iron or steel casing is less inert and a likely source of iron in water samples. Since PVC is more likely to break or be damaged at the ground surface where it may be exposed to vehicles or implements, the PVC casing can be enclosed at the surface in a protective iron housing or other housing, such as one of concrete, which will provide equivalent protection.

An additional problem with PVC casing arises when well depths exceed much more than 150 ft. Proper completion using grout (discussed later) can cause collapse of the casing string due to excessive pressure. Where elevated temperatures can be expected. this problem is magnified.

Screen Slot Size. Well screens allow water to enter the well without material from the borehole wall. A sieve analysis is usually run on the aquifer materials to be monitored. In general the slot size should retain 50% or more of the zone material.

If the well is used just for monitoring, a smaller screen size opening may be chosen with little adverse effect. If feasible, a gravel pack should be considered. Screens should be selected to minimize water entrance velocities and thereby avoid chemical changes due to rapid changes in the partial pressure of the water being sampled (Johnson Division, U. O. P., 1980)

Grouting and Sealing. Water well technology has borrowed much from the petroleum industry in the field of well cementing. Unfortunately, the water well industry does not have the equipment on the shallow well drilling rigs that is capable of implementing the innovations that the petroleum and geothermal industries have developed. Nonetheless, water wells can be sealed to the same standards of petroleum wells using care and proper techniques.

In grouting or sealing a well, the annular space between the well casing and the borehole sides is filled with an impermeable material, usually some form of clay or cement. Various techniques have been established for injecting or placing grout in wells; the selection depends on the equipment available (Campbell and Lehr 1973). Selection of the method for drilling a monitoring well is highly important to ensure that the best representative samples can be collected at the most reasonable cost. Several choices are available regarding drilling techniques and equipment. The choice should be made in light of geologic condition in the site and the type of chemical constituents to be analyzed for. Suggested references on drilling methods are contained in Campbell and Lehr (1973) and U.S. EPA (1977)

Well Drilling and Development. In "developing" a well, steps are taken to ensure that water will easily flow into the well. This is essential if the well is to be bailed prior to testing. At least five methods are used to improve well capability: surging, jetting, blasting, acidizing, and hydraulic fracturing. Some of these methods may be extreme for a monitoring well, but all are technically feasible and should be considered when planning well completion (Johnson, Division, U. O. P., 1980).

Well Security. The monitoring well should be equipped with a locking system, which easily can be installed on the iron casing placed over the well casing. A simple padlock usually is adequate.

Placement

Placement of monitoring wells is a complex, site-specific process because each geothermal development has unique geologic, hydrologic, and topographic features. Monitoring wells can be located in three different demographic sections: 1) isolated or remote areas, 2) urban/suburban areas and 3) predominantly agricultural areas. In all areas the wells must be placed so that any excursion of contaminants can be detected. Specifically, wells should be placed down gradient of potential contaminant sources and close enough to the sources that early detection is possible, yet far enough away to overcome the probability of missing an excursion due to low dispersion characteristics of the aquifer system.

Isolated Areas. Isolated areas are those areas that are undeveloped as to resources (other than perhaps grazing or timber harvest) and are sufficiently far away from cities or towns that special effort must be taken to reach the site. Commonly, little is known about the "shallow" geohydrologic system in such areas, which makes the proper placement of wells difficult.

Definition of the "shallow" groundwater system will be determined in conjunction with drilling initial monitoring wells. Where little data are available to aid in determining groundwater flow direction and gradients, wells should be placed so that direction and gradient can be determined. A minimum of three wells are required to ascertain these parameters. Topography is a primary tool to be used in well location. Unconfined groundwater systems are generally subdued replicas of the surface topography. Thus, by careful reference to maps of appropriate scale, wells may be located with high probability of success.

In mountainous regions, care must be taken to ensure that wells are located within the same drainage basin. This is especially difficult because of the bedrock nature of most mountain sites. Wells should be placed so as to intercept and make use of any structural or depositional features such as foliation, stratification, cleavage, jointing, or faulting which may play an important role and influence the flow of groundwater.

A thorough hydrogeologic investigation can provide sufficient data to eliminate the need for any groundwater monitoring in some areas, and will point out the areas and locations requiring concentrated effort. It must be kept in mind that igneous and metamorphic rocks may have very low permeability and porosity making completion of an adequate sampling well in these rock types very difficult. At the same time, these parameters tend to increase the rate at which a contaminant will move under a given hyraulic gradient.

In remote areas where the geothermal resource underlies alluvial materials and the local groundwater system consists of flow through sand and gravel aquifers, the geohydrologic survey will delineate the most appropriate drilling sites.

Agricultural Areas. The relatively flat ground used in some agricultural areas is commonly underlain by low gradient groundwater flow systems. Perturbations on the flat water table surface that are caused by site activities conceivably could cause mounding which would lead to radial flow away from the source.

As a part of the site geohydrologic survey, an inventory of existing irrigation, domestic, and public supply wells should be made. Water level measurements and pumpage data along with aquifer parameter information will allow determination of the most probable flow direction and travel time in the event of a contaminant excursion. Records of existing wells are also useful in providing possible locations for sampling background conditions.

Monitoring well locations in agricultural areas should be selected to provide the most representative samples possible. Wells should be placed so that contaminant migration can be detected in any likely direction. Special attention needs to be given to any surface disposal activity. In areas of greatest concern, where groundwater exists at near-surface depths, wells will be relatively inexpensive and easy to install, so these facilities can be readily monitored. Where groundwater is deep, monitoring well expense will be much greater, and a detailed geohydrologic study will provide the most cost-effective means of good monitoring coverage.

Urban Areas. Monitoring networks in urban and suburban areas will be subject to both positive and negative influences. The most positive aspect will be a network of improved roads which will provide ready access to the most favorable sampling locations. However, land ownership and access rights may cause legal difficulties beyond the technical aspects of well placement. The multitude of potential transport paths for groundwater contaminants in the urban/suburban environment make monitoring a complex issue.

A complete and thorough geohydrologic survey of the proposed development site is essential. Domestic and public supply wells within a radius of at least 1 mile should be inventoried. Background chemical data should be obtained from public supply wells and any domestic wells where it is available. Water level measurements will provide a good basis for determining groundwater flow direction. Data from the geohydrologic survey will provide the input necessary for optimal location of monitoring structures. Monitoring wells should be placed in all important aquifers potentially affected by geothermal development. This will increase costs but provide the necessary data to provide for protection of producing supply aquifers.

5.3 SAMPLING TECHNIQUES - SATURATED ZONE

Geothermal monitoring historically has not included monitoring of overlying aquifer systems. If monitoring is undertaken at a special location, it will be necessary to establish the precautions to be taken from well design through sample analysis. When a sample methodology is to be selected, all personnel who will use the data should be consulted.

1. Laboratory personnel need to know what analysis is desired; how many samples need to be run; the number of duplicates to perform; the level of accountability needed; and what are the proposed methods of physically collecting the sample.

2. Analysts should be consulted on the statistical precision or significance to be achieved in terms of frequency, spatial distribution, and temporal distribution.

3. Field collection personnel need to be consulted to ensure that the available collection equipment is suitable for collecting samples that can be analyzed for the parameters selected.

Groundwater sampling equipment procedures have been described by Scalf et al. (1981) and Gibb et al. (1981). Certain guidelines provide a framework for designing a sampling program. Prior to equipment acquisition, parameter selection, or other work, the objective of the sampling program must be clearly spelled out. For example: Is the injection well contaminating any other aquifer? Does the contamination have to be proven? If so, what level of statistical certainty must be achieved? To establish a recognizable trend in a certain contaminant to prove or show that an aquifer is being contaminated the size of sample needed (how many), the frequency that the samples must be taken (how often), and the spatial location of the samples (where) must be determined.

Very often there is not a large enough data base to decide with certainty the statistically best sampling methodology. In this case, the best approach is to "shotgun" the samples sites; i.e., assume that the observations are independent and that analysis of the random sample will provide enough information for further sampling refinement. A good reference for statistically designing a monitoring program can be found in Ground Water, November-December (Nelson 1981).

Once the number of samples, frequency of samples, and relative location of samples has been decided, an iterative process should begin in which the cost of sampling is weighed against the validity of the results. This step usually is needed to ensure that the entire sampling program is feasible in terms of cost and sample results. If the costs are too high to allow adequate samples to be taken, then a management decision must be made as to increasing the funding or cutting back the sampling program.

The relative locations of sampling sites are determined on the basis of local geology, hydrology, topography, and the statistical needs of the analysis. The actual locations of the wells is clearly more a factor of the site limitations and limitations of the drilling equipment.

Once a sampling program has been chosen, laboratory and field personnel should also be consulted as to the most appropriate sampling devices and storage procedures. Table 5.1 gives a summary of sampling devices. Methods are described in the following subsections. Regardless of the sampling device being used, the following guidelines for well development and sampling are designed to provide consistent and usable results.

1. Each monitoring well should be pump tested for 2 or 3 hours. The data collected can be used to help determine sampling frequency and the rate and period of time that each well should be pumped prior to sample collection.

2. Three to five well volumes of water should be pumped prior to sample withdrawal. The rate and time of the pumping should be determined on the basis of the transmissivity of the aquifer and the well diameter.

3. The choice of pumps can be made on the basis of the sensitivity of the chemical indicators. Air or nitrogen lift pumps are not recommended unless the tests performed are pH insensitive with no volatile chemical constituents. Peristaltic or submersible pumps are recommended, with a bailer being a second choice.

4. Field tests for pH, dissolved oxygen, temperature, conductivity, etc. should be performed as quickly as possible. Any questions should be directed to the laboratory personnel or the Standard Methods for the Examination of Water and Wastewater (APHA 1980).

TABLE 5.1. ADVANTAGES AND DISADVANTAGES OF SAMPLING TECHNIQUES

System	Advantages		Disadvantages
Bailers	Simple Low cost Efficient	No air contact	Require relatively large well Hole must be vertical Winch needed for deep wells
Peristaltic pumps	Medium cost Simple operation Accurate control of flow cross Low potential for cross contamination	No air contact	Requires power source Low flow volume
Piston pumps	Medium to high cost Simple High flow volume	No air contact	Generally requires power source
Centrifugal pumps	High flow volume	No air contact	Requires large power source High cost
Nitrogen lift	Simple Low cost		Gas contact - possible contamination
Air Lift	Simple Low cost		Gas contact
Vacuum	Simple Low cost	No air contact	Limit to 8 m pull partial pressure chemistry changes

5.3.1 Sampling with a Bailer

Sample Point

Sample points can be located wherever the well diameter is large enough to accommodate the bailer. Limitations include wells that are bent or too twisted.

Summary

The bailer is equipped with a check or flap valve that allows water to enter the device. The bailer is lowered into a well on a cable or rope. The bailer is usually constructed of iron or PVC pipe with the valve located at the lower end. As the bailer fills with water, the valve opens; when the bailer is removed from the water being sampled, the valve closes. This technique is reliable and inexpensive (Johnson Division, U.O.P. 1980). A commonly used bailer is called the "Kemmerer Sampler" and is described by Scalf et al. in the Manual of Ground-Water Sampling Procedures (1981).

Equipment/Supplies

Bailer, hoist mechanism (drill rig, winch, etc.), sample containers, preservative

Documentation Necessary

Well location, depth to water, sample device, name of sampler, date, time, volume of sample, analyses to be performed, volume of water purged from system

Procedure

Prior to sampling make certain that all equipment is clean. Measure depth to water and calculate volume of well. Lower bailer to a depth below the water surface if possible. Raise the bailer and empty the water (the volume of the bailer should be known). Repeat the process until three to five volumes of water have been removed from the system. Allow the well to recover. Insert the bailer and withdraw a sample. Transfer the contents of the bailer to the sample container with as little contact to the air as possible. If metals are to be analyzed, use a PVC bailer.

5.3.2 Sampling with a Peristaltic Pump

Sample Points

Sample points can be located wherever a tube can be lowered into a well or other water source. Limitations include depths greater than 8 m and wells where large volumes of water must be removed to purge the well.

Summary

A peristaltic pump sequentially contracts a flexible hose and causes a partial vacuum. The pump can move a very precise amount of water or other liquid and is easily operated, easily sanitized, inexpensive, and reliable.

Equipment/Supplies

Peristaltic pump, tygon tubing, sample containers, preservative, measuring container. Optional Equipment: straight tubing to lower into well.

Documentation Necessary

Well location, depth to water, sample device, sampler, date, time, volume of sample, analyses to be performed

Procedure

Prior to sampling make certain that all equipment is clean. Measure depth to water with steel tape. Calculate volume of well. Insert tubing to a depth 4 in. below the water level. Insert discharge tube into premeasured container. Pump three to five volumes of water from the well - this may require lowering the tube to keep it below the water surface. Allow well to recover. Insert discharge tube into the sample container; the tip of the tube must be below the water surface in the container as it fills.

5.3.3 Sampling with Air or Nitrogen Lift Systems

Sample Point

Air or nitrogen lift samplers can be used on almost any type or depth well as long as the well diameter is sufficient to insert piping. The major limitations are the volumes of air or gas necessary with deeper depths.

Summary

An air or nitrogen lift system consists of a double tube system in which the water is pumped by forcing air up through it. The system theoretically can be used at almost any depth. As air is forced down one tube and up the other, the water in the tube is pushed to the surface. Gas analyses may prove to be inaccurate and pH and metal values may be inaccurate.

Equipment/Supplies

Airlift sampling device consisting of the proper length of tubing, air or gas source adequate to move water to the surface, sample containers, and preservatives.

Documentation Necessary

Well location, depth to water, sample device, sampler type, gas source and type of gas, volume of sample, name of sampler, analyses to be performed.

Procedure

Prior to sampling make certain that all equipment is clean. Measure the depth to the water and calculate the volume of the well. Pump three to five volumes of the well water. During purging, adjust pumping rate to allow for sample collection. Depending on the apparatus, place a section of tubing on the outflow pipe of the pump housing. Insert tubing into sample container and fill with tube below water surface.

5.4 SAMPLING TECHNIQUES - VADOSE ZONE

The same planning and precautions necessary for the saturated zone are required for the vadose zone which is defined as the subsurface zone lying between the land surface and the permanent water table. The zone includes partially saturated materials but also some saturated materials in "perched" conditions. Care must be taken so that the sampling program maximizes the information gained from the investigation.

There are three types of water movement in the partially saturated zone: infiltration across the soil surface and through the topsoil; movement in perched water tables; and movement in the partially saturated zones.

The water movement in the topsoil usually occurs in an unsaturated state where the soil water is at less-than-atmospheric pressures (Everett 1976), which can be measured by tensiometers. Soil texture, initial water content, and soil stratification affect the infiltration capacity. Curves showing the relationship between soil depth and water content with time after cessation of infiltration (drainage profiles) for a given soil can be used to determine the rate of outflow. Salinity and solution composition can affect water movement greatly.

Perched water zones may be discovered by neutron logging (discussed later) or upon examination of stratigraphic data. Water movement in perched water table zones is measured as in saturated zones with piezometers. Small-diameter pipes are driven, augered, or jetted into the known or suspected saturated zone and the water levels in the pipes are measured. The pipes must have a tight contact with the soil. The slope of the groundwater level measured in three or more piezometers will indicate the direction of lateral water movement.

Monitoring water movement and quality in the partially saturated zone is an extension of soil monitoring techology. The American Society of Agronomy (Black 1965) and Wilson (1980) have compiled detailed descriptions, specifications, and methods of many techniques. Of primary interest are flow rates to the water table and the storage capacity of the materials above the water table.

5.4.1 Collecting Soil Samples

Soil samples can be taken to obtain extracts of soil water to establish soil texture distribution, water content and chemistry, and the bulk density or water release curves. Land samplers, such as post-hole augers, screw or sleeve-type augers, or power-driven augers, are useful in obtaining samples to characterize texture, water content, and chemistry. Small-diameter tubes may be driven to desired depths to obtain a texture distribution. Larger diameter core samples, hand- or power-driven, are used to determine bulk density.

A "bucket" type hand auger can cut core sizes from 2 to 4 in. in diameter. Extensions may be added inexpensively for deeper sampling. Hand-driven soil sampler systems include soil sampling tubes (4 to 16 ft in length), a drop hammer, and a tube puller jack. Deep wells (Section 5.3) may be necessary to sample throughout the partially saturated zone.

Sample Points

There are no absolute criteria for sample points. Points that should be considered include production well sites, monitoring well sites, construction sites, and other excavations where subsurface soil samples can be obtained for low costs. Once the geothermal and monitoring sites are established, soil sample sites should be located close to areas where contaminated water is present.

Summary

Soil analysis can be valuable as a monitoring tool for tracing leachate constituents, particularly those prone to cation exchange or other adsorption reactions. Soil cores near a geothermal site can be collected during well installation. Techniques for core collecting are available, and methods for soil analysis are documented (U.S. Dept. Interior 1977). Sulfate (SO_4), chloride (Cl), and nitrate (NO_3) are soluble and unaffected by cation exchange reactions in soil. This results in mobility impeded only by the restrictions of water movement. Soil samples can be analyzed for these anions in addition to cations which are generally more strongly associated with the solid soil matrix. Because cations must be released from the solid matrix prior to determination, analysis is more difficult. However, zone location of heavy metals or phosphorus accumulations can only be detected through soil analysis.

Analytical Methods

Pore water extraction can be accomplished by either pressuring the sample to force water out; drying and collecting the water vapor; hydraulically crushing the sample and collecting the water; or applying a negative pressure (vacuum) to extract water. The water collected is subjected to the standard laboratory techniques for analysis.

Equipment/Supplies

Soil samples collected during drilling can be cores taken with a split spoon sampler or a shalby tube. Near-surface samples can be collected with a hand auger. Field equipment should provide a sample that is compatible with the laboratory equipment.

Documentation

Each sample should be logged into the field notes as to location, depth, description of zone or formation that sample is from, collection technique, name of collector, date, and time.

Procedure

Prior to sampling, all equipment should be scrupulously cleaned. If a shallow core sample is to be taken using a hand auger, surface litter and contaminated materials should first be removed. Once the sample is removed from the ground, it should be placed in the proper preservation/transportation container as soon as possible. Make certain that the material is not contaminated by hands, gloves, or other equipment.

If a sample is to be collected by a drill core, cleanliness is again essential to the procedure. Drill rigs are usually covered with oil and grease that can contaminate the hole, the sampler, and the samples. Make certain that the driller does not lubricate any of the moving parts immediately before sampling depth is reached. If possible, clean the sample tube with distilled water prior to sampling. Use clean gloves to handle all equipment. Note: laboratory personnel can provide the best advice on sample handling and preservation.

5.4.2 Collecting Soil-Water Samples

Soil-water samples can be obtained for analysis with the porous ceramic cups similar to those used in tensiometers. These soil-moisture samplers, called suction or pressure-vacuum lysimeters, allow repeated sample collection from a single installation and appear to be the best tool available for sampling partially saturated moisture (Everett 1981).

Salinity sensors are available for in situ evaluation of soil salinity but should not be used at soil-water pressures less than -2 atmospheres. They are most accurate in gauging changes in salinity rather than exact concentrations (Black 1965).

Sample Point

Sample point selection for pressure-vacuum lysimeters is the same as for soil core samples.

Summary

Pressure-vacuum lysimeters are used to obtain samples of in situ soil moisture. In the most improved form, this device consists of a porous ceramic cup capable of holding a vacuum, a small-diameter sample accumulation chamber of PVC pipe or other inert material, and two sampling tubes leading to the surface. The lysimeter is placed at the desired sampling depth. A vacuum is applied to the system and water from the soil surrounding the lysimeter gradually accumulates in the sampler. The vacuum is released and pressure is applied forcing the water to the surface through the sampling tube. This sampler will function when the soil moisture tension is between 0 and 0.8-bar. Thus, the soil moisture tension should be measured with a tensionmeter to ensure that samples can be obtained to prevent unfruitful attempts at sampling by this method.

Analytical Methods

The water sample from a pressure-vacuum lysimeter can be analyzed for the same consituents as a surface water sample except for suspended solids and gases. The volume of sample that can be obtained at a single sampling period with one lysimeter is often very limited (maybe less than 155 ml) and thus can be a limitation on the chemical analysis schedule to be performed. However, more than one lysimeter could obviously be used in a location to get more sample volume. The solids are usually filtered out by the sand pack around the cup and gases tend to be released during the vacuum phase of sample collection.

Equipment/Supplies

Pressure-vacuum lysimeters can be purchased from a number of manufacturers (see Groundwater Monitoring Review)(a) or can be manufactured using 2-in. PVC pipe and ceramic cups. Other materials needed are clean, fine-grained, silica sand, sealing clay or cement, tubing to go from the lysimeter to the surface (heavy wall tygon works well), a vacuum/pressure source (hand pump or electric), and suitable sample containers. Assorted clamps and other hardware are needed to clamp off tubing to take the samples. It is recommended that the surface access to a lysimeter or lysimeter nest be protected in the same fashion as a monitoring well. A large-diameter pipe should be cemented over the tubing with a locking cap installed to protect the sampling tubes and to more easily locate the sample sites at a different time.

Documentation

Documentation should be the same procedure as for core sampling.

Procedure

Parizek and Lane (1970) provide a detailed description of lysimeter installation and sampling:

Placement holes are first drilled to the desired depth. They may be 101 to 152 mm (4 to 6 in.) in diameter depending upon the number of lysimeters to be placed in each hole. A plug of wet bentonite clay is placed in the bottom of the hole to isolate the lysimeter from the undisturbed soil below it. This plug is optional. A layer of crushed, pure silica sand of almost talcum powder consistency (such as Super Sil), at least 152 mm (6 in.) deep, is placed on top of the bentonite. This layer is used to provide a clean transmission medium for soil moisture moving under capillary pressure, to ensure hydraulic contact of the adjacent soil medium with the porous tip, to fill uneven voids created during drilling, as well as to prevent clogging of the ceramic tip by colloids, organic matter, or soil particles. The lysimeter is placed in the hole to the desired depth, and the silica sand is placed around it until the lysimeter is half buried. Native soil, free from pebbles and rocks, is backfilled and tamped with long metal rods. After the lysimeter is covered with about 152 mm (6 in.) of soil, a second plug of bentonite is deposited to further isolate the lysimeter and to guard against possible channeling of water down the drill hole. Backfilling is continued with native soil to the depth where it is desired to set the next lysimeter, at which point the above procedure is repeated.

(a) National Water Well Association
500 W. Wilson Bridge Rd.
Worthington, Ohio

The typical sampling procedure is as follows:

1. The lysimeter's discharge tube is clamped shut and a vacuum is applied to the "in" tube.
2. A vacuum of about 460 mm (18 in.) of mercury is applied and clamped off.
3. The lysimeter is held at this negative pressure for a sufficient period to obtain the amount of fluid desired.
4. The pressure is returned to normal; the discharge tube is opened; and the "in" tube is directed into the sample container.
5. The lysimeter can be used to collect another sample by starting with step 1 again.

5.4.3 Nonsampling Methods

Methods available for determining water content or storage capacity often have the capability to simultaneously monitor water movement. The three most commonly used methods to infer partially saturated flow employ tensiometers, psychrometers, and neutron moisture logging. Soil-water content and/or soil-water pressure can be measured by these methods and by electrical resistance blocks.

Neutron moderation or moisture logging requires an access well installed by augering and driving a tube (a driven well point) for shallow depths (to 150 cm) or by standard drilling techniques for greater depths. A tight fit between the borehole and casing is necessary to minimize water migration via the annulus. Drilling mud should not be used (as required by jetting or augering) because it will interfere with water content observations. A high concentration of fast neutron moderators (e.g., boron or chlorine) in the subsurface may cause errors in water content determination. A soil-water characteristic curve can be used to translate water contents into soil-water suction values, and therefore hydraulic head gradients, to enable the estimation of water movement direction.

Tensiometers measure soil-water pressures during partially saturated flow. Arrays of tensiometers must be installed to detect horizontal water flow. Psychrometers are necessary for soil-water pressure measurements below -1 atmosphere. Electrical resistance blocks are used to measure soil-water content, and therefore pressure, if provided with suitable soil-water characteristic curves. This method is comparatively inexpensive.

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6.0 QUALITY ASSURANCE

Good quality data is not automatic. Qualified and trained personnel, accurate procedures, proper selection and maintenance of equipment, and independent verification of results are some of the contributing factors to an effective quality assurance (QA) system. This section introduces some of the principles and practices of quality assurance and laboratory quality control that can contribute to the quality objectives of a monitoring program. It is suggested that a plant can establish an appropriate and efficient quality assurance program by evaluating Sections 6.1 and 6.2 along with the local environmental concerns. With this balance, proper emphasis can be applied to those elements in Sections 6.3 and 6.4 to arrive at a responsive quality assurance program.

This section deals, in part, with detecting out-of-control situations via the chemical results and describes the necessity to decide on an appropriate response. However, each plant must establish a response that is compatible with the local environmental problems and regulations.

6.1 QUALITY ASSURANCE SENSITIVITY

Based on the results of two interlaboratory round-robin comparisons (Karkalits and Hankins 1981; Kindle and Woodruff 1981) and the input from geothermal practitioners during the course of the investigation leading to this report, the variability and scatter of resulting data, including the technical procedures, was estimated (Table 6.1). This estimated sensitivity is directed

TABLE 6.1. QUALITY SENSITIVITY

Potential for Data Scatter	Constituent/Parameter	Plant Sampling Location
High	Hydrogen sulfide/sulfide ion, fluoride, mercury, aluminum, silver	Two-phase flow locations, cooling tower emissions
Medium	Cadmium, arsenic, zinc, chromium, lead, manganese, copper, barium, sulfate, pH	Steam lines, gas lines, solid sampling
Low	Ammonia, chloride, radon, lithium, boron, silica, total dissolved solids, alkalinity, conductivity	Single-phase liquid locations

strictly at the variability of the results and not at the severity of environmental concern. This gradation can serve as a first guide to establishing an efficient balance in the portion of a geothermal emissions QA program that is directed at maximizing reproducibility of concentration values. Since geothermal situations cover a broad spectrum, this information is intended only as an approximate guide. Nitrate, molybdenum, and selenium were not part of the round-robins and are not ranked.

6.2 QUALITY ASSURANCE FOR GEOTHERMAL PLANT MEASUREMENTS

In taking an overall look at the needs for quality in a geothermal measurement program, the following steps need to be addressed.

1. Establish procedures.
2. Determine the effort to be expended in a quality program.
3. Place control of the entire monitoring program with one person.
4. Quantify sampling error.
5. Calculate the mass and charge balances of the analytical data.
6. Calculate mass balance water and gases move through the plant.
7. Consider a one-time/occasional review by a geothermal chemist.

1. Establish Procedures. Procedures should be adopted for:
   a. Sampling and Preservation
   b. Analysis
   c. Evaluating quality control (precision, accuracy).

This manual and the cited references should be of major assistance in this area. It is not suggested that every fluid constituent or sampling location addressed in this manual needs to be monitored at every plant. The monitoring program should reflect the needs dictated by the individual plant or local environmental regulations.

2. Quality Program Effort. Although a rule of thumb is that 10% of the measurement effort should be devoted to QA, the geothermal plant case is different. In one regard the specific time demands for quality may be eased if the entire QA program described here is adopted. The calculation of a mass throughput for the entire plant showing where the entering pollutants leave provides a baseline check on the overall results. If the ratio of two sample concentrations taken from different points in the plant changes relative to this baseline, then a flag is raised to determine the cause. Also, a review of the characterization program by a (external) geothermal chemist provides some additional assurance of technical problem avoidance. Establishing hard data on the sampling variability will permit the quality program to balance the needs and focus on the weakest link.

Most importantly the demands for quality program effort are not uniform with time. Figure 6.1 shows a conceptual level of effort for a geothermal quality program as a function of time.

3. One Person Control. In order to assure continuity and logic it is recommended that one person have authority for the entire chemical monitoring effort. It is further recommended that, in a routinely operating plant, the person(s) who analyzes the sample be the person who takes the sample.

4. Quantify Sampling Error. Unlike analytical laboratory determinations, geothermal sampling occurs under conditions of minimum standardization, at least to date. Discrete samples should be collected as a function of sampling rate (and sample probe position, if a movable probe is utilized) and analyzed to determine the sampling variability at the particular plant location. This uncertainty is then compared with various other uncertainties, such as total flow or analytical uncertainty, to achieve a balance for the quality effort (and the total monitoring program). This comparison is needed only once but should be performed under normal plant operating conditions.

5. Mass Charge Balance of Data.

6. Plant Mass Balance. It is recommended that a mass throughput balance be calculated for the entire plant once steady operation is reached. This calculation will permit the establishment of normal concentration values for particular emission streams and normal ratios between release points. Any deviation from these values may well flag a situation that requires additional check to determine the cause of the change. It can perform a check on the quality of the entire monitoring program and can indicate minor plant operating upsets.

7. Monitoring Program Review. It is suggested that each operating geothermal facility will find it cost- and quality-effective to have the monitoring program individually reviewed by an experienced geothermal chemist.

6.3 QUALITY ASSURANCE PLAN

A Quality Assurance Plan, usually in the form of a checklist, is one method that can be used to define the specific requirements that apply to different components of a multidimensional project.

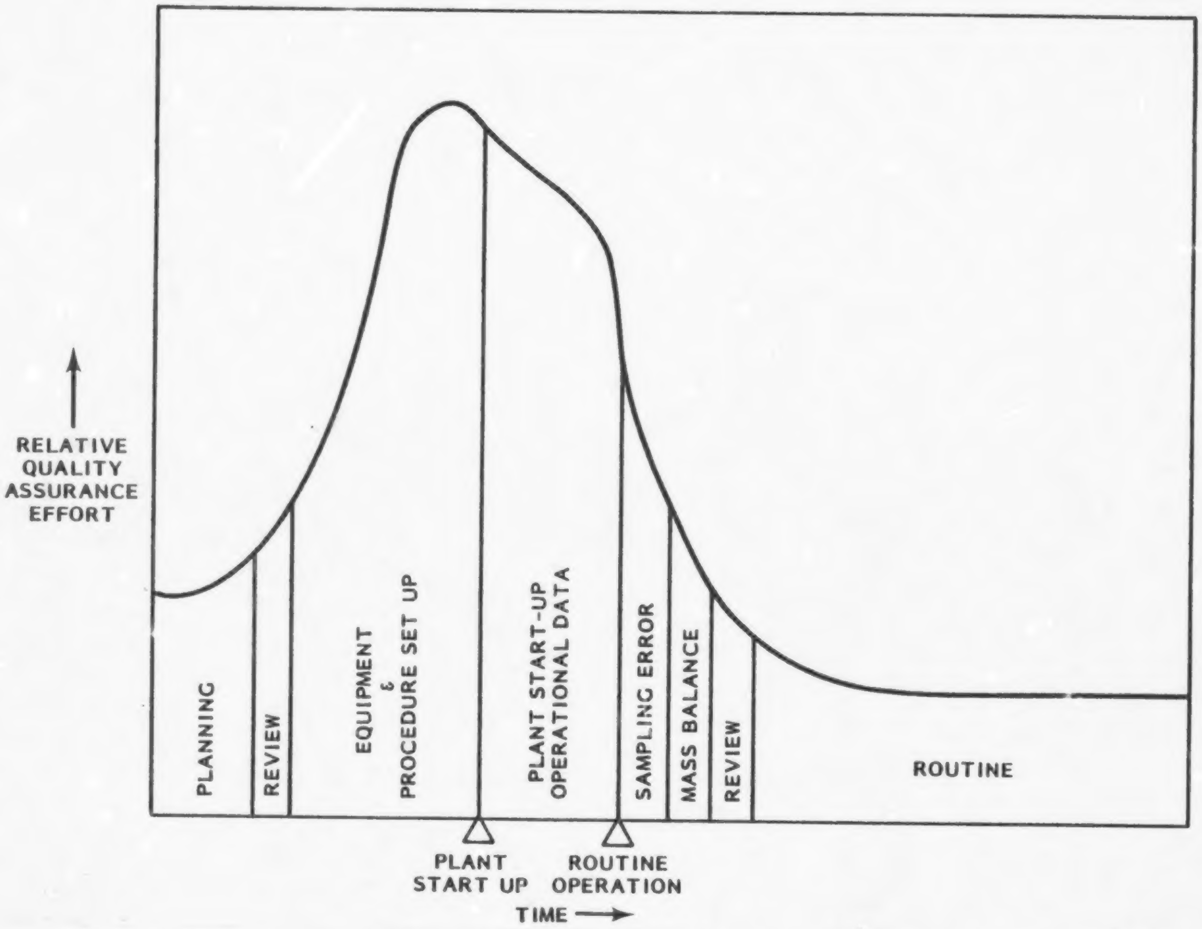

FIGURE 6.1. Quality Assurance Effort for Emission Monitoring as a Function of Time (conceptual)

6.3.1 Written Procedures

Each person should be adequately trained for the job assignment. Written standard operating procedures are excellent tools for training new personnel and achieving the desired standard of performance. In an analytical laboratory, a procedure must be sufficiently detailed to assure that two individuals performing the same analysis produce equivalent results. If there is any possibility of different results, the procedure should be written more explicitly. Although it may be sufficient for plant operational needs to reference a standard method from a documentable source (where highly trained or professional people do the work), it is preferable to have the procedure outlined as to how it applies to the particular laboratory/sample mix.

The outline of a written quality assurance plan may include (some or all) of the following items as appropriate:

1. Title
2. Method Summary
3. Analytical Range
4. Precision
5. Sample size
6. Sample care
7. Sample preparation
8. Reagents
9. Equipment
10. Equipment calibration
11. Equipment calibration check
12. Equipment clean up
13. Quality control checks (acceptable values)
14. Instrument detection limits
15. Units of measure
16. Calculations
17. Reporting and format requirements
18. Potential interferences
19. What to do if a problem arises
20. Alternative analytical method
21. Safety measures
22. References

In all cases, a written procedure must reflect how the analysis is actually being performed. If there are changes in technology and techniques, reviews should be frequent to assure that the procedures are accurate representations of performance. The information can be documented on the procedure itself or some other means traceable to the documents themselves.

Occasionally, deviations from a procedure are necessary, i.e., contaminated sample, insufficient quantity, equipment malfunction, an attempt to increase sensitivity, or an attempted improvement in method. Any significant deviations used and the reasons for them must be documented. If the change in procedure is to be performed frequently, a new formal procedure should be issued.

6.3.2 Document Control

Each standard operating procedure should be identified at a minimum with Title, Date authorized, Prepared by, Authorized by, Page _____ of _____, and Revision Number or Date. If a procedure involves multiple pages, each page should be identified at a minimum with Title (or Code Number), Revision Number (or date), and Page _____ of ____.

A minimum frequency for review should be yearly, or whenever procedures are modified. Each standard operating procedure should be located at or near the work station to provide easy access to those performing the work. Previously issued procedures should be destroyed, with the exception of copies needed to retain a history of how the procedure has been modified and improved.

6.3.3 Sampling

Good data begins with good sampling, which begins with appropriate planning. In other words, all personnel involved in actual sample collection, sample analysis, data evaluation, and reporting should be consulted to determine their needs and a sampling plan prepared.

In order to assure that all necessary information is documented, a sample identification sheet which supplies the appropriate information should be prepared. This sheet should include:

1. Sample identification
2. Collected by
3. Date
4. Time
5. Well identification
6. Specific sample location
7. Sampling equipment
8. Comments
9. Rate of flow
10. Duration of prior flow
11. Pressure of flow
12. Temperature of flow
13. Field analysis
14. Preservation steps

Any field data collected should be identified as such. All field observations should be recorded in a bound field log book. Anyone evaluating the data should be able to easily distinguish field data from the laboratory work.

A numbering system must be developed to uniquely identify each sample collected; then data can be traced forward and backward from any point in the process. If a sample data sheet is used, the sample itself must be labeled with sufficient information, in a permanent manner, to provide correlation to the more complete data sheet.

The written procedure for sample collection should address:

1. Sample location
2. Preliminary requirements such as prior flow
3. Details of how to perform the collection
4. What preservation methods are necessary
5. What field tests should be run
6. Transport requirements
7. Data to be recorded during sampling
8. What other information needs to be recorded, where, and how.

Delivery of samples to an offsite laboratory should be documented. A log could provide a means of traceability between field sample number and a laboratory accession number if the laboratory uses its own identification system.

6.3.4 Calibration

All analytical equipment (both field and laboratory) should be calibrated on a regular basis as specified in the quality assurance plan. Calibration should include traceability of the standards used to the National Bureau of Standards, a natural physical constant, or other nationally recognized standard including those commercially prepared. Routine calibration checks can be performed using "working standards" that are available from plant laboratory supplies. Calibration should be performed according to written procedures and documented. Records should be maintained as described in 6.3.6. In the case of in-plant instruments, calibration should be checked and recorded each day of operation, as a minimum. For the better assurance of quality data, instrument calibration should be checked before and after the analysis.

6.3.5 Discrepancy Reports

A discrepancy reporting procedure should be adopted for significant variations (the criteria to determine significance are to be established for a particular plant based on the local environmental sensitivities). A discrepancy report should include the requirement, the discrepancy, and the resulting required action. The benefit of documenting discrepancies is that a variety of events can be examined to determine if there are any previously unapparent unifying factors. Also, sufficient documentation is supportive in justifying changing a procedure or pointing out what particular aspect of a procedure needs more quality control. The discrepancy report should follow the sample through analysis and, most importantly, data evaluation.

A corrective action does not have to be performed every time an item is identified as discrepant. However, discrepancies should be evaluated for indication of any "trends."

6.3.6 Records

The documentation should be permanent and recorded in ink or in another unalterable form. There should be enough correlation between records to answer who, what, when, why, and how on any measurement. Records should flow in a chronological order. When defining the retention period for records, the following considerations are recommended.

1. What records are needed (for plant use; for public record; for audit)?
2. How long after the performance may verification of the original data be required?
3. What records may be needed to review and to seek an explanation of an indeterminant change?

It is suggested that records relating to the original constituent mass balance through the plant, sampling uncertainties, and initial analytical qualification (set-up) be kept until they are superceded. Routine monitoring results may be important to retain to demonstrate good plant performance, but the back-up documentation leading to those routine results seems to be less important. If an operating plant has a rigorously followed discrepancy reporting procedure (6.3.5), the requirements for routine data record keeping may be quite reasonable.

6.3.7 Audits

Quality Assurance involves constant communication. An audit is one accepted method for supplying an independent, timely, and appropriate evaluation of how well the system is working. The formality may vary from an official audit by an outside agency to an inhouse review. An effective audit should disclose any inadequacies in the basic interpretation of quality requirements and failures to comply with procedural instructions.

The two common types of audits are: 1) the adequacy audit, which evaluates how well the established QA program fulfills the goals or requirements, and 2) the compliance audit, which evaluates how well personnel are complying with the established requirements and procedures. The QA audit is not only a method of verifying the QA program's effectiveness but is a very vital action. By exposing any deficiencies, the QA program itself can be improved.

An audit should be performed to a written checklist based upon the established written requirements. The audit report should be issued to those responsible for corrective actions and the appropriate levels of management.

6.4 LABORATORY QUALITY CONTROL

Laboratory Quality Control (QC), a subset of quality assurance, has two major functions: 1) determining quality and 2) controlling quality. The laboratory analyst and supervisor are responsible for establishing the methods of control to assure the integrity of the work.

For quality control in the analytical laboratory, some recommended quidelines are:

- The purity of reagent chemicals should be related to the sensitivity and specifications of the required analysis. When not specified by the method it is best to employ reagent grade.

- Reagents must be prepared and standardized against reliable primary standards. These reagents must be restandardized or prepared fresh as often as required to assure stability.

- Regularly check stock and working standards for signs of deterioration, e.g., discoloration, precipitation, change of concentration.

- All reagents and solutions should be properly labeled as to compound, concentration, solvent, date of preparation, date of expiration and preparer.

- Primary standards should be obtained whenever available from reliable sources such as
  National Bureau of Standards
  Office of Standard Reference Materials
  Institute of Materials Research
  Washington, D.C. 20234
  (301) 921-2045
  or other chemical supply companies. Documentation should be obtained and retained which describe the measurements (analyses), the methods/sources used to determine the measurements, and the uncertainties of

the measurements performed on the standard(s) furnished. Once received, these primary standards should be properly stored and then prepared in calibrated volumetric glassware and stored in properly labeled containers that will not alter the essential characteristics of the reagent.

- For metal analysis, all standard reagents used for atomic absorption or emission spectroscopy should be of spectral quality.

6.4.1 Analytical Control Checks

Chemicals may vary from one source to another, lot to lot, and even within lots. An easy way to control this determinant error is to have a regular check program where each new reagent is run in conjunction with the previous source and a comparison made. When a new primary standard, or dilution thereof is introduced, it is recommended that both the old and the new standards be analyzed and the results statistically analyzed (by the conventional t-test) to check for agreement before accepting the new standard. A discrepancy here should be documented, at a minimum, and a new standard or an investigation may be appropriate.

If an analysis involves solutions that deteriorate rapidly, a good procedure is to use reagent blanks as a quick check. A method blank should be processed each time an analysis is run. To run a method blank, follow the procedure, step by step, with the exception of adding an appropriate substitute for the actual sample to be analyzed, and check for interference at the final step. If the cumulative blank interferes at the final assay point, try to eliminate or reduce the interference to a nominal level. If the interference cannot be eliminated or reduced, its magnitude must be considered in the calculation of final concentration of the analyte being assayed. The number of blanks to be run within a method depends upon the stability of method performance (baseline drift) and the total number of samples to be run consecutively. In some methods, for example, atomic absorption, the method blank is automatically and continuously compensated for by the constant flow of reagents through the nebulizer.

Each series of analyses should include applicable elements of the following:

1. Initial calibration or verification that the calibration is still within tolerances. This step could be as simple as checking the absorbance or transmittance on a spectrophotometer after the periodic calibration is completed. Or, an EPA Quality Control Solution or NBS Standard Reference Material 1643a could be run for trace element analysis. This check should be performed at the beginning and end of each series of analyses, or at least once a day for stable instruments used in routine plant operation.

2. Method Blank Analysis. This blank should be used to indicate any inherent interferences due to the actual procedure itself.

3. Spiked Sample Analysis. This effort should provide information on whether or not the sample matrix is affecting the measurement methodology. For geothermal brine samples, particularly concentrated samples, this approach and/or the use of matrix-matched standards is important and recommended.

4. Duplicate Sample Analysis. These data can be used to evaluate long-term precision of a method. The relative percent difference (RPD) is recorded:

$$RPD = \frac{D_1 - D_2}{(D_1+D_2)/2} \times 100$$

where RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value.

5. Continuing Calibration Verification. Sometimes referred to as a "control check," this verification step can be a dilution of the original calibration solution, an EPA Quality Control Solution, National Bureau of Standards-Standard Reference Material, a commercially supplied standard (control check), or an inhouse prepared standard (working standard).

The above sample values should be recorded and analyzed to provide an evaluation of the accuracy and precision for the analysis work. The American Society for Quality Control defines these variables as follows:

Accuracy - The difference between an average value and the true value when the latter is known or assumed.

Precision - Relative to the data from a single test procedure, the degree of mutual agreement among individual measurements made under prescribed conditions.

When a process or system is new, it will require more frequent quality control checks in order to define the accuracy and precision that can be expected. Once a history is developed and documented it is the responsibility of those concerned to decide what periodic systematic checks must continue to be performed in order to verify the validity of new data.

6.4.2 Charge Balance

It is recommended that a charge balance be calculated for each significant aqueous sample where a complete analysis is available. This step ensures that all of the major cations and anions are accounted for and that the sample calculates as electrically neutral, which it must be. Errors of 5 to 10% in this charge balance are common and may exceed that for relatively clean waters (and particularly steam). Calculating the charge balance checks the laboratory analysis of major components. Thus, as a quality indicator for pollution emissions, its value is limited to the major components. To calculate a charge balance the form in Figure 6.2 can be used.

6.4.3 Out-of-Control Determination

The ability to detect of out-of-control situations is necessary to ensure that environmental consequences of plant operation are satisfactorily established. Concerning the plant emissions, an out-of-control situation could be

CHARGE BALANCE

PARAMETER	ANIONS			PARAMETER	CATIONS		
	mg/ℓ	Factor	(meq/ℓ)		mg/ℓ	Factor	(meq/ℓ)
HCO_3^-		0.0164		NH_4^+		0.167	
$CO_3^=$		0.0333		Ca^{++}		0.0499	
HS^-		0.0302		Fe^{++}		0.0358	
$SO_4^=$		0.0208		K^+		0.0256	
F^-		0.0526		Li^+		0.144	
NO_3^-		0.0161		Mg^{++}		0.0823	
$HPO_4^=$		0.0208		Na^+		0.0435	
Cl^-		0.0282		Sr^{++}		0.0228	
TOTAL		☒		TOTAL		☒	

$$\text{CHARGE BALANCE} = \frac{\text{meq/l anions}}{\text{meq/l cations}} = \_\_\_\_\_ =$$

FIGURE 6.2. Charge Balance Worksheet

either one that is different from normal operation (which can be detected by the techniques described below or by plant operational conditions) or one that results in an emission above permissible levels (which is determined by comparison with local regulations).

Several methods are used to determine if a laboratory result is different from the normal value. Frequently, the operator or analyst is familiar with the normal value and mentally evaluates the result as part of the analysis/report sequence. It is recommended that a more formal approach be taken for sensitive emmissions. The use of running averages, particularly when plotted on a graph along with the actual data, is another approach that can detect both abrupt and gradual changes. Comparison of the ratios of two analytical values for different sampling locations, (such as described in Section 6.2 for using plant mass balance determinations) can also signal an apparent change in the status quo.

Control Charts

Any of the above methods should be accompanied with or incorporate a control chart, and for the most critical parameters at a specific geothermal plant and location, the environmental monitoring effort should include a control chart to graphically document performance and trends. As with the other parts of this Quality Assurance Section, the control chart should be blended into a QA plan that reflects the needs of the specific plant. A control chart is a good way to document consistency of performance.

In the 1920s, Dr. W. A. Shewhart of Bell Telephone Laboratory developed the theory of control charts as a visual indication of the quality of manufactured products. The purpose of control charts is to detect "assignable causes" of variation in a process. Process variations are of two kinds: 1) random, i.e., due solely to chance and 2) assignable, i.e., due to a specific cause. Theoretically, all variation should be random and could be defined as being "in a state of statistical control." The statistics Dr. Shewhart plotted were

$$\text{Standard Deviation} = S = \sqrt{\frac{\left(\sum_{i=1}^{n} X_i^2\right) - \left(\sum_{i=1}^{n} X_i\right)^2 / n}{n-1}}$$

$$\text{Range} = (R) = (\text{the largest } X_i) - (\text{the smallest } X_i)$$

$$\text{Arithmetic Mean} = \bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

The elements common to his control charts are illustrated in Figure 6.3.

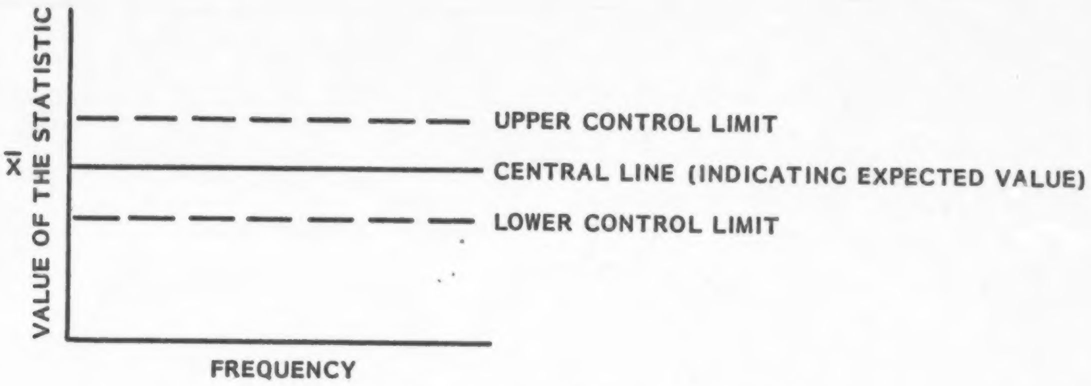

FIGURE 6.3. Shewhart Control Chart

Inherent in environmental analysis is the problem of variability in true concentration of samples. The accuracy of the testing method must be evaluated indirectly with the recovery of spikes and standards. Control charts could be used to indicate the standard reference value and the acceptable variation of that analysis.

Two replacements for the Shewhart $\bar{X}$ control charts could serve to illustrate the accuracy of recovery of different standards or spikes. The first is the cusum (cumulative sum) control chart. Its plotted points include information from all observations prior to and including the point itself. Unlike the Shewart control chart the control limits vary. The EPA Region VI QC manual (1972) describes a cusum chart using the square of the difference between observed and true values.

The second method is simply a modification of Shewhart's technique to evaluate the percent recovery instead of X.

$$\text{Percent recovery} = 100\,\frac{\text{observed}}{\text{known}} = P$$

$$\text{Average Percent Recovery} = \bar{P} = \frac{\sum_{i=}^{n} P_i}{n}$$

$$\text{Standard Deviation for percent recovery} = S = \sqrt{\frac{\left(\sum_{i=1}^{n} P_i^2\right) - \left(\sum_{i=1}^{n} P_i\right)^2 / n}{n-1}}$$

7.0 SAFETY ASPECTS

7.1 SAMPLING

Each sampling location can have hazards that may be unsuspected by an inexperienced operator. The major hazards include the following.

- High Temperatures - The piping will be very hot.
- High Pressures - High pressure can lead to burns or injury from flying missiles if failures occur.
- Scalding Fluids - Any leak during sampling could permit scalding steam or brine to escape.
- Toxic Gases/Noncondensable Gases (NCG) - Toxic (H_2S) or non-life supporting (CO_2, N_2) gases are present in all geothermal gases. Potential trouble spots may include the lines carrying NCG from the first separator or the condenser.
- Flammable Gases - Some geothermal gases contain sizeable fractions of CH_4 indicating that there may be a fire hazard once the gas mixes with air.
- Unstable Ground - Unstable ground may be associated with brine treatment ponds, drilling residues or geothermal features, whether natural or man-made. Appropriate cautions are site specific.
- Component Failure - There have been at least four cases from the mid 1970s to 1982 where components containing geothermal brine or steam have burst or have been broken. Three deaths and shrapnel injuries have occurred. Two of the incidents and all three fatalities were associated with drilling activities. However, three of these instances were directly related to corrosive attack. Certain stainless steels are susceptible to stress cracking in the presence of chloride ion (as in brine). Mineral acids, if used for routine scale control, can dissolve carbon steel.

7.2 LABORATORY ANALYSIS

Usual safety precautions should be followed.

APPENDIX

40 CFR 146, Subpart F

146.51 Applicability

This subpart sets forth Criteria and Standards for underground injection control programs to regulate all injection not regulated in Subparts B, C, D, and E (Class I, II, III, and IV wells).

(a) Generally, wells covered by this Subpart inject non-hazardous fluids into or above formations that contain underground sources of drinking water. It includes all Class V wells but is not limited to those types of injection wells.

(b) It also includes wells not covered in Class IV that inject radioactive materials listed in 10 CFR Part 20, Appendix B, Table II, Column 2, and injection wells used to store hydrocarbons which are gases at standard temperature and pressure.

146.52 Inventory and Assessment

(a) The owner or operator of any Class V well shall, within one year of the effective date of an underground injection control program, notify the Director of the existence of any well meeting the definitions of Class V under his control and submit the inventory information required in 40 CFR 122.37(c)(1).

(b) Within three (3) years of approval of the State program the Director shall complete and submit to EPA a report containing:

(1) The information on the Construction features of Class V wells, and the nature and volume of the injected fluids.

(2) An assessment of the contamination potential of the Class V wells using hydrogeological data available to the State;

(3) An assessment of the available corrective alternatives where appropriate and their environmental and economic consequences; and

(4) Recommendations both for the most appropriate regulatory approaches and for remedial actions where appropriate.

40 CFR 122.37(c)(1)

As part of the inventory, the Director will require at least the following information:

(1) Facility name and location
(2) Name and address of legal contact
(3) Ownership of facility
(4) Nature and type of injection wells and
(5) Operating status of injection wells

Note: This information is requested on national form "Inventory of Injection Wells," OMB No. 158-R0170.